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Global distributions of a large number of halocarbons, hydrocarbons, SF_6 and N_2O are presented. These data are complemented with measurements in the polluted environments to establish urban-nonurban relationships and daily doses of these species. Measurements conducted over a 3-year period show that the atmospheric burdens of CCl_2F_2, CCl_3F, and CH_3CCl_3 are increasing rapidly. The growth of CCl_4 is small and that of N_2O is essentially undetectable. Long residence times of CCl_2F_2 and CCl_3F rule out the existence of any major removal processes in the troposphere. The global distribution of CCl_2F_2 and CCl_3F is used to calculate a fast inter-hemispheric exchange rate of 1.2 years. CCl_4 was shown to have an important oceanic sink, while both CH_3Cl and N_2O have a major source in the ocean. CH_3CCl_3 atmospheric data was used to demonstrate that its long residence time makes it a potential depletor of stratospheric ozone. The hydroxyl radical concentration in the troposphere was shown to be significantly lower ($\simeq 4 \times 10^5$ molec./cm^3) than previously believed and probably asymmetric in the two hemispheres. Measurements show that the troposphere contains slightly under 3 ppb of organic Cl and about 77 percent of this is of man-made origin. The organic Br and I abundances are much lower and much less certain. The troposphere contains about 1 ppb of organic F and all of it appears to be man-made.

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ATMOSPHERIC DISTRIBUTIONS, SOURCES AND SINKS OF SELECTED HALOCARBONS, HYDROCARBONS, SF_6, AND N_2O

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ABSTRACT

Global distributions of a large number of halocarbons, hydrocarbons, SF_6, and N_2O are presented. These data are complemented with measurements in the polluted environments to establish urban-nonurban relationships of these species. Atmospheric growth rates of selected species are characterized based on measurements conducted between 1975 and 1978.

Results indicate that inert man-made species are relatively uniformly distributed in the global atmosphere, while the more reactive species show significant interhemispheric gradients. Atmospheric residence times of 65 to 70 years for fluorocarbon-12 and 40 to 45 years for fluorocarbon-11 best fit the observational data. These residence times rule out the possibility of any major removal mechanisms in the troposphere. Between 1975 and 1978 fluorocarbon-12 and fluorocarbon-11 concentrations in the troposphere increased at an average rate of 22 ppt/year and 14 ppt/year, respectively. The global distribution of fluorocarbon-12 and fluorocarbon-11 was used to establish a relatively fast average interhemispheric exchange rate of 1.2 years. Unlike fluorocarbons, carbon tetrachloride appears to have an oceanic sink that was found to be about half as effective as the stratospheric sink. A major source of methyl chloride, sufficient to account for nearly all the atmospheric methyl chloride, was identified as the ocean. Atmospheric measurements of methyl chloroform support an 8- to 11-year residence time. These long residence times would allow a significant amount of methyl chloroform to enter the stratosphere, thus making it a potentially important depletor of stratospheric ozone. A long methyl chloroform residence time suggests serious disagreement with global models and points to reduced average hydroxyl radical (HO) concentrations of only 3×10^5 to 4×10^5 molecules/cm^3. In addition, methyl chloroform global distribution supports southern hemispheric HO values that are a factor of 1.5 or more larger than northern hemispheric values. These HO values were used to estimate the residence times of a large number of molecules.

Measurements show that the troposphere contains slightly under 3 ppb of organic Cl and about 75 percent of this is of man-made origin. The organic Br and I contents are much lower and much less certain. The troposphere contains about 1 ppb of organic F and all of it appears to be man-made.

The Pacific Ocean (45°N - 45°S) was found to be a significant source of N_2O despite the high oxygen content in the South Pacific. This oceanic flux, when extrapolated to global waters, suggests an oceanic N_2O source of 20 to 30 million tons (N_2O)/year (13 to 19 million tons (N)/year). The atmospheric residence time of N_2O was found to be very long ($20 \text{ years} < \tau_{N_2O} < 120 \text{ years}$). During this study, no detectable increase in atmospheric N_2O was observed. Measurements in urban-suburban locations were used to characterize daily doses of the measured chemicals, many of which are suspected to be highly toxic.

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SECTION 1

INTRODUCTION

Over the past two decades, an increasing number of hazardous chemicals has been released into the environment. Many of these chemicals persist in the atmosphere for such long periods of time that they bring about nearly permanent changes in the biosphere. Others are found to be hazardous to human health and are responsible, at least in part, for the rising cancer rates in the industrialized countries.

The primary group of pollutants of interest in this study was halogenated organics, although other halogenated as well as nonhalogenated species (such as SF_6, N_2O, light hydrocarbons, and CO) were also studied. Halogenated organics are important atmospheric constituents for a number of reasons. Halocarbons that are stable in the troposphere (such as fluorocarbons-12, -11, -113, -114 and carbon tetrachloride) are suspect as precursors of stratospheric ozone-destroying chlorine atoms. Vinyl chloride has been linked to angiosarcoma and is possibly mutagenic. Many chloroethanes and methanes are suspect as potential human carcinogens. In addition, atmospheric halocarbons and nitrous oxide absorb infrared heat radiation, and these may exacerbate the warming effects caused by CO_2.

It should be added that the same chemicals that threaten to cause global pollution are tracers that can provide valuable information about the dynamics and the chemistry of the natural atmosphere.

The present study was therefore launched to develop information on the composition of the clean and the polluted atmosphere to determine the distribution, sources, and sinks of a large set of pollutants of interest.

SECTION 2

OVERALL OBJECTIVES

The overall objectives of this study were:

- To characterize the burden of selected trace constituents such as halocarbons, hydrocarbons, SF_6, N_2O, O_3, NO_x, and CO in the clean troposphere and the polluted urban environments.
- To determine the atmospheric distributions of selected halocarbons, hydrocarbons, SF_6, and N_2O in the northern and the southern hemispheres.
- To determine the growth rates, residence times, sources, and sinks of the trace constituents of interest.
- To analyze measured atmospheric data, along with other available information, to understand better the dynamics and the chemistry of the global atmosphere.

SECTION 3

SUMMARY OF MAJOR FINDINGS AND CONCLUSIONS

A number of conclusions with wide-ranging implications to our understanding of atmospheric chemistry were derived from the conduct of this study. The following are some of the salient results:

- Global analysis of carbon tetrachloride (CCl_4) emissions data since 1914 showed that atmospheric CCl_4 was predominantly of man-made origin, contrary to the prevalent view that CCl_4 was largely of natural origin (Singh et al., 1976a).
- Phosgene was measured for the first time in the urban and the clean atmosphere and its sources and sinks were characterized (Singh, 1976; Singh et al., 1977c).
- The global distribution of a comprehensive set of reactive and inert trace constituents was measured. The average concentrations in the northern hemisphere, the southern hemisphere, and the globe are summarized in Table 1. We demonstrated that relatively inert trace constituents (such as fluorocarbons-12, -11, -113, -114; CCl_4, SF_6, N_2O) are well-mixed within each hemisphere and the average concentration in the southern hemisphere differs only marginally (10 to 15 percent lower) from the northern hemisphere values. More reactive man-made species (such as CH_3CCl_3, C_2Cl_4, $CHCl_3$) were found to have more pronounced hemispheric gradients (Singh et al., 1979a). Global distributions of many species (e.g., F-113, F-114, CH_3Cl, CH_3CCl_3, and C_2H_6) were obtained for the first time.
- Average atmospheric growth rates of important chlorocarbons (and N_2O) were characterized based on field studies conducted between 1975 and 1978. These are summarized in Table 2.
- Unlike other reactive chlorinated organics, methyl chloride was shown to possess no north-south concentration gradient. This implied a large natural source. We collected data from the Pacific Ocean and identified in the ocean a major source of methyl chloride (3 million tons/year) sufficient to account for nearly all of the atmospheric methyl chloride (Singh et al., 1979a).
- The distribution of fluorocarbons-12 and -11 was used with the global emissions data to establish quantitatively a mean interhemispheric exchange rate of 1.2 years (Singh et al., 1979a).
- The residence times of fluorocarbons-12 and -11 were shown to be so long (40 to 45 years for fluorocarbon-11 and 65 to 70 years for fluorocarbon-12) as to rule out the possibility of any significant

Table 1

AVERAGE BACKGROUND CONCENTRATIONS OF IMPORTANT ATMOSPHERIC TRACE CONSTITUENTS

Compound	Major[†] Source	Concentration[*]		
		Northern Hemisphere Average	Southern Hemisphere Average	Global Average
N_2O	N	311 ppb	311 ppb	311 ppb
CCl_2F_2 (F-12)	A	230 ppt	210 ppt	220 ppt
CCl_3F (F-11)	A	133 ppt	119 ppt	126 ppt
CCl_2FCClF_2 (F-113)	A	19 ppt	18 ppt	18 ppt
$CClF_2CClF_2$ (F-114)	A	12 ppt	10 ppt	11 ppt
$CHClF_2$ (F-22)	A	20-30 ppt	--	--
$CHCl_2F$ (F-21)	A	5 ppt	4 ppt	4 ppt
SF_6	A	0.31 ppt	0.27 ppt	0.29 ppt
CCl_4	A	122 ppt	119 ppt	120 ppt
CH_3CCl_3	A	113 ppt	77 ppt	95 ppt
CH_3Cl	N	611 ppt	615 ppt	613 ppt
CH_3I	N	2 ppt	2 ppt	2 ppt
CH_3Br	A, N	5-20 ppt	--	--
$CHCl_3$	A	14 ppt	≤3 ppt	8 ppt
CH_2Cl_2	A	44 ppt	20 ppt	32 ppt
C_2HCl_3	A	16 ppt	<3 ppt	8 ppt
C_2Cl_4	A	40 ppt	12 ppt	26 ppt
C_2Cl_6	A	≤5 ppt	--	--
CH_2BrCH_2Br	A	≤5 ppt	--	--
CH_4	N, A	1430 ppb	1390 ppb	1410 ppb
C_2H_6	N, A	1060 ppt	524 ppt	792 ppt
C_2H_2	A	<200 ppt	<200 ppt	<200 ppt

[*] For those species where significant latitudinal variations within the hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed in the hemisphere, represents the total burden of the species in that hemisphere. The concentration data are for late 1977: ppt = 10^{-12} v/v; ppb = 10^{-9} v/v.

[†] N = Natural; A = Anthropogenic.

Table 2

AVERAGE ATMOSPHERIC GROWTH RATES OF SELECTED SPECIES FROM 1975 TO 1978 IN THE NORTHERN HEMISPHERE

Compound	Average Growth Rate*
N_2O	<1 ppb/yr
CCl_2F_2 (F-12)	22 ppt/yr
CCl_3F (F-11)	14 ppt/yr
CCl_4	3 ppt/yr
CH_3CCl_3	15 ppt/yr

*Based on data collected between 30°N - 40°N.

tropospheric sinks that may prevent these species from entering the stratosphere almost in their entirety (Singh, 1977a; 1977b; Singh et al., 1979a).

- We demonstrated for the first time that the methyl chloroform residence time is 8 to 11 years, contrary to the belief based on model predictions that methyl chloroform residence time must be 1 to 2 years. This new information suggested that 15 to 20 percent of all methyl chloroform released at ground level could enter the stratosphere (Singh, 1977a, 1977b; Singh et al., 1979a) thus making methyl chloroform a potential depletor of stratospheric ozone.
- The utility of using methyl chloroform as an indicator of the hydroxyl radical (HO) abundance was recognized. We showed that the global average HO abundance was about 3 to 4 × 10^5 molecules/cm^3, or about a factor of 5 lower than that predicted by models. This finding has wide implications for all classes of species for which reaction with HO is the dominant removal mechanism. Thus, it appears that a large number of chemicals persist in the atmosphere for significantly longer periods that previously believed.
- Methyl chloroform distribution in the northern hemisphere and the southern hemisphere also supports the view that the HO abundance in the southern hemisphere is at least 1.5 times more than in the northern hemisphere. We inferred that higher levels of carbon monoxide (CO), an effective sink for HO in the northern hemisphere, are the reason for this asymmetry. Increasing CO emissions in the future have the potential to deplete further the scavenging ability of the atmosphere (Singh, 1977b).

- We demonstrated that the oceanic sink for CCl_4 can provide an atmospheric turnover time of about 100 years, thus making this sink about half as effective as the stratospheric sink (Singh et al., 1979a).
- Nitrous oxide (N_2O) was shown to have a uniform concentration in the northern hemisphere and southern hemisphere and an atmospheric residence time of greater than 20 years (Singh et al., 1979b).
- We found a dominant source of N_2O in the Pacific Ocean. The global oceanic source was quantified to be 20 to 30 million tons (N_2O)/year (Singh et al., 1979b).
- No change in the atmospheric abundance of N_2O was detectable during the three-year period of this study.
- The total organic halogen budgets were determined and are summarized in Table 3. These contradict free chlorine levels of greater than 3 ppb (max 8 ppb) that have occasionally been reported in the upper stratosphere. It is clear from Table 3 that man-made activities have already significantly perturbed the global atmosphere.

Table 3

TROPOSPHERIC CHLORINE, BROMINE, IODINE AND FLUORINE ORGANIC BUDGETS

Species	Budgets			Percentage Source Contributions	
	Northern Hemisphere	Southern Hemisphere	Global Average	Natural	Man-Made
Cl	2.9 ppb	2.4 ppb	2.7 ppb	23	77
Br	10-30 ppt	--	--	50-90	10-50
I	<2 ppt	<2 ppt	<2 ppt	100	0
F	1.0 ppb	0.9 ppb	1.0 ppb	0	100

- We determined levels of a large number of halogenated pollutants by conducting field experiments at several characteristic urban sites. Many of the chemicals are either highly toxic or suspected carcinogens. The human intake (dose) of these chemicals was quantified.
- Results from this study allowed us to provide our best estimates for the seasonally averaged atmospheric residence times of a large number of molecules. These are given in Table 4.

Table 4

BEST ESTIMATE OF THE SEASONALLY AVERAGED ATMOSPHERIC RESIDENCE TIME OF SELECTED MOLECULES BASED ON RESULTS FROM THIS STUDY

Molecule	Mean Atmospheric Residence Time, τ (years)	Major Sinks*	Major Source
CCl_2F_2	65	S	A
CCl_3F	40	S	A
CH_3Cl	2.7	T,S	N(O)
CH_2Cl_2	1.0	T	A
$CHCl_3$	1.2	T	A
CCl_4	≥ 25 (<40)	S,O	A
$CHFCl_2$	4.3	T,S	A
CHF_2Cl	34.8	S,T	A
CH_2ClF	3.3	T,S	A
CH_3Br	2.9	T,S	N(O),A
CH_4	21.5	T,S	N,A
CO	0.6	T	N,A
CCl_2CCl_2	0.8	T	A
$CHClCCl_2$	0.04	T	A
CH_3CCl_3	8.3	T,S	A
CH_2ClCH_2Cl	0.6	T	A
CH_3CHCl_2	0.5	T	A
CH_3CH_2Cl	0.3	T	A
CH_3CF_2Cl	50.6	S	A
CH_2BrCH_2Br	0.6	T	A
C_2H_6	0.5	T	A,N
N_2O	>20	S	N(O)
COS	1.6	T	U
CS_2	0.4	T	U

S-stratosphere, T-troposphere, O-oceans, A-anthropogenic, N-natural, U-unknown

*In the instance more than one symbol is defined; the first symbol represents the dominant sink, the second symbol represents a less important sink. The latter sink is identified only if it contributes at least 5% to the total loss. Unless otherwise identified in parentheses, the tropospheric sink is due to reaction with hydroxyl radical. The percentage of material released at ground level that will enter the stratosphere is estimated to be between 2τ to 2.5τ. For $\tau>40$ years nearly all of the material will enter the stratosphere.

SECTION 4

ANALYTICAL METHODOLOGY

A. Trace Constituents of Interest

We attempted to measure as many halogenated compounds of interest as possible. These were complemented by measurements of other nonhalogenated species that may affect the chlorine chemistry of the stratosphere. Table 5 gives the list of chemicals that were measured during the conduct of this study in urban, suburban, and background environments. For all halogenated species, N_2O, and organic nitrogen compounds, electron-capture gas chromatography was the primary means of analysis. The hydrocarbons and CO were measured using flame-ionization gas chromatography. Continuous chemiluminescent instrumentation was used for the analysis of O_3, NO, and NO_2.

B. Experimental Procedures

1. Air Analysis

Because of the extremely high sensitivity of the electron-capture detector (ECD) a number of species listed in Table 5 can be measured with a direct 5-ml injection of air. In general, however, preconcentration of samples was necessary. We chose to use as small a sample size as necessary to measure a maximum number of chemicals of interest on a given GC column. In no case did a sample volume of more than 500 ml have to be used. The cryogenic trapping of air was conducted in 1/16 in. diameter stainless-steel traps packed with a 4 in. bed of glass beads or glass wool. During sampling these traps were maintained at liquid oxygen temperature. The actual volume of the sample was measured at the cryogenic trap exit. The collected aliquot was thermally desorbed and injected directly into the GC. Both electrical heating and hot water desorption techniques were used for injecting the trapped sample and both were found to be satisfactory. A typical sample size was 250 ml. Because of the dominant water response of the ECD, a post-column

Table 5

CHEMICALS MEASURED IN THE CLEAN TROPOSPHERE AND IN THE PACIFIC OCEAN

Compound Name	Chemical Formula	Measured in	
		Air	Sea Water
Fluorocarbon-12	CCl_2F_2	x	x
Fluorocarbon-11	CCl_3F	x	x
Fluorocarbon-22	$CHClF_2$	x	
Fluorocarbon-21	$CHCl_2F$	x	
Fluorocarbon-113	$CClF_2CCl_2F$	x	
Fluorocarbon-114	$CClF_2CClF_2$	x	
Sulfur hexafluoride	SF_6	x	
Carbon tetrachloride	CCl_4	x	x
Chloroform	$CHCl_3$	x	x
Methylene chloride	CH_2Cl_2	x	
Methyl chloride	CH_3Cl	x	x
Methyl iodide	CH_3I	x	x
Methyl bromide	CH_3Br	x	
Hexachloroethane	CCl_3CCl_3	x	
Methyl chloroform	CH_3CCl_3	x	
Ethylene dibromide	CH_2BrCH_2Br	x	
Tetrachloroethylene	CCl_2CCl_2	x	
Trichloroethylene	$CHClCCl_2$	x	
Phosgene	$COCl_2$	x	
Nitrous oxide	N_2O	x	x
Nitric oxide	NO	x	
Nitrogen dioxide	NO_2	x	
Peroxyacetyl nitrate (PAN)	$CH_3\overset{\overset{O}{\parallel}}{C}OONO_2$	x	
Peroxypropionyl nitrate (PPN)	$CH_3CH_2\overset{\overset{O}{\parallel}}{C}OONO_2$	x	
Ozone	O_3		
Carbon monoxide	CO	x	
Methane	CH_4	x	
Ethylene	C_2H_4	x	
Acetylene	C_2H_2	x	
Ethane	C_2H_6	x	
Propane	C_3H_8	x	
Butane	C_4H_{10}	x	
Pentane	C_5H_{12}	x	

Ascarite trap was inserted to remove water for halocarbon analysis. No water trap was used for the analysis of N_2O, peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and phosgene.

The ECDs were maintained at 325°C because we discovered that in most cases the ECD response increased with an increase in temperature. In the case of PAN, PPN, and phosgene, the EC-GC coulometer was maintained at 30°C. For these species, the reduced temperature seemed to give the best response. A number of GC columns were used during the conduct of this study. Table 6 shows the columns that can adequately be utilized for the separation and analysis of these chemicals. Table 6 also shows the recommended columns for routine analysis. The other columns listed in Table 6 were mainly used for identification purposes. In addition, the identiy of chemicals was confirmed by determining their EC ionization efficiency as well as EC thermal response. Methyl chloride identity was further established by GC/MS analysis. The light hydrocarbons were measured by employing standard methods from the literature (Westberg et al., 1974). Details of these measurement methods have already been provided (Singh et al., 1977d; 1978d) and need not be repeated here.

Figures 1-6 provide representative chromatograms for the atmospheric separation of selected species. The separation and analysis procedures for light hydrocarbons are well documented (Westberg et al., 1974).

2. Water Analysis

As shown in Table 5, we also performed water analysis for a limited number of species, namely fluorocarbons-12 and -11, CH_3Cl, $CHCl_3$, CCl_4, CH_3I, and N_2O. In the initial stages of the research effort a large volume of water was purged with ultrapure helium at a very slow flow rate. The outcoming helium, which was in equilibrium with the water content, was analyzed and this concentration reported. In the latter stages (third year) of this project, most of the water analysis was performed aboard ship. For this cruise, we devised additional quantitative techniques.

The analysis on the seven selected chemicals in seawater (Table 5) was conducted by quickly enclosing a 25-ml volume of seawater and an equal volume

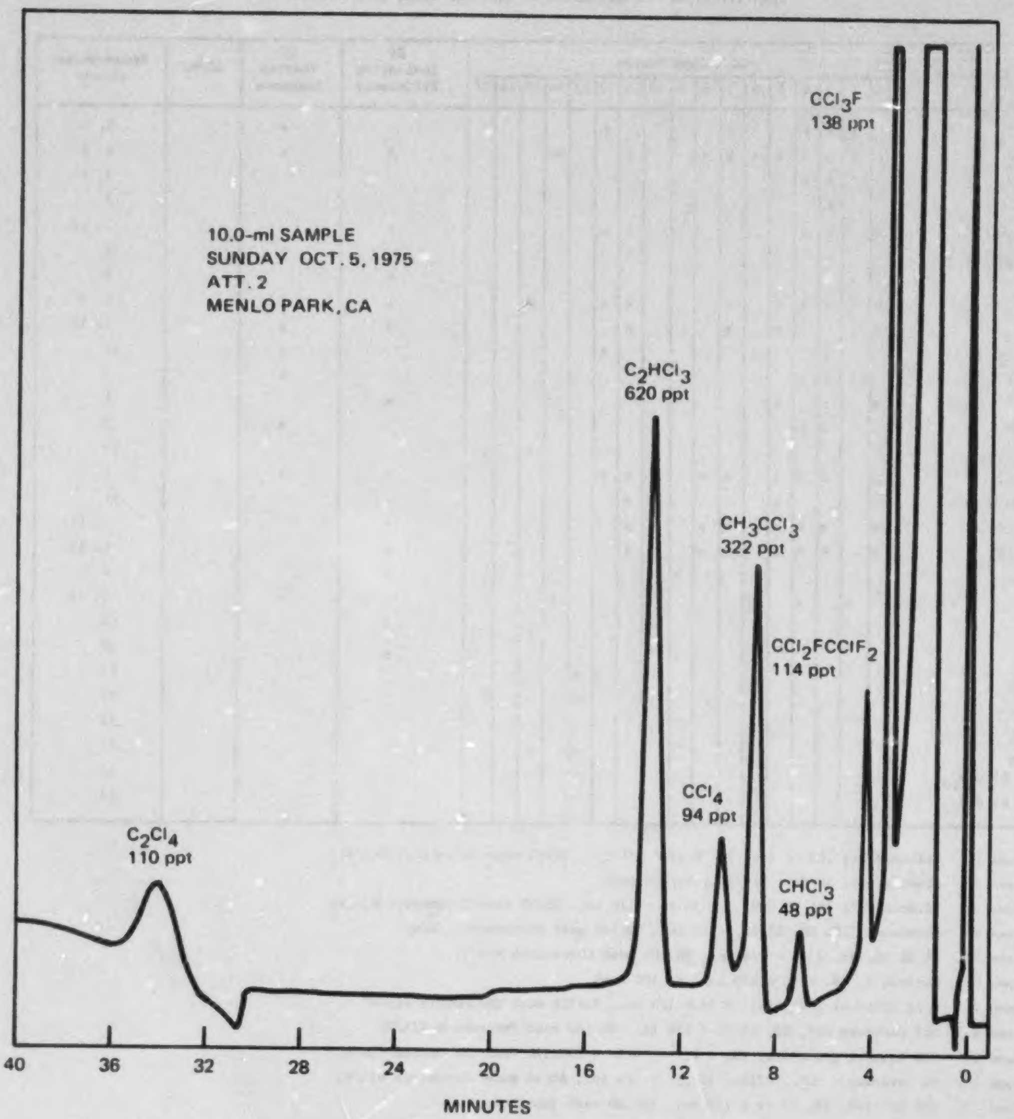
Table 6

IDENTIFICATION AND SEPARATION OF SELECTED TRACE CONSTITUENTS

Chemicals	GC Column Number																	EC Ionization Efficiency	EC Thermal Response	GC/MS	Recommended Column
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17				
CCl_2F_2		x	x	x		x	x					x							x		3, 4
CCl_3F	x	x	x	x	x	x	x	x			x			x				x	x		3, 4
$CHClF_2$			x	x																	3, 4
$CHCl_2F$			x																		3
$CClF_2CCl_2F$	x		x	x							x	x						x			3, 12
$CClF_2CClF_2$			x								x								x		3
SF_6		x				x												x			2
CCl_4	x		x	x	x		x				x	x			x			x			1, 3
$CHCl_3$	x				x		x				x							x	x		1, 11
CH_2Cl_2			x									x							x		12
CH_3Cl			x	x															x	x	3
CH_3I	x		x		x													x			1
CH_3Br			x	x															x		3
CCl_3CCl_3															x						15
CH_3CCl_3	x		x	x	x		x	x			x	x						x	x		1, 3
CH_2BrCH_2Br					x						x										11
CCl_2CCl_2	x		x	x	x		x	x			x							x			1, 11
$CHClCCl_2$	x		x	x	x		x	x			x							x			1, 11
$COCl_2$									x									x			9
N_2O		x		x		x								x					x		2, 14
PAN										x								x			10
PPN										x								x			10
C_2H_6													x								13
C_2H_4													x								13
C_2H_2													x								13
C_3H_8													x								13
(n, i) C_4H_{10}													x								13
(n, i) C_5H_{12}													x								13

Column 1.	Silicone oil 10% DC 200, SS, 6 ft × 1/4 in., 30/60 mesh Chromosorb W(A/W)
Column 2.	Alumina, SS, 20 ft × 1/8 in., 80/100 mesh
Column 3.	Silicone oil 20% DC 200, SS, 30 ft × 1/4 in., 30/60 mesh Chromosorb W(A/W)
Column 4.	Chromosil 310, SS, 15 ft × 1/4 in., 80/100 mesh Chromosorb W(A/W)
Column 5.	5% SE 30, SS, 7 ft × 1/4 in., 80/100 mesh Chromosorb W(A/W)
Column 6.	Porapak Q, SS, 6 ft × 1/8 in., 80/100 mesh
Column 7.	0.4% Carbowax 1500, SS, 15 ft × 1/4 in., 80/100 mesh Chromosorb W(A/W)
Column 8.	10% Carbowax 400, SS, 10 ft × 1/4 in., 80/100 mesh Chromosorb W(A/W)
Column 9.	30% Didecyl phthalate, SS, 5 ft × 1/4 in., 100/120 mesh Chromosorb P(A/W)
Column 10.	5% Carbowax × 400, Teflon, 10 in. × 1/4 in., 60/80 mesh Chromosorb W(A/W)
Column 11.	20% SP-2100, SS, 15 ft × 1/8 in., 80/100 mesh Supelcoport
Column 12.	Carbopack C/0.2% CW 1500, SS, 6 ft × 1/8 in., 80/100 mesh
Column 13.	Durapak n-octane/porasil C, SS, 15 ft × 1/8 in., 100/120 mesh
Column 14.	Porasil B, SS, 10 ft × 1/8 in., 100/120 mesh
Column 15.	5% SE-30, SS, 3 ft × 1/8, 100/120 mesh Chromosorb W(A/W)

All columns maintained at 40°C, carrier flow rate 30 to 40 ml/min, ECD temperature 325°C except in case of PAN, PPN and $COCl_2$ where it is 30°C.



10.0-ml SAMPLE
SUNDAY OCT. 5, 1975
ATT. 2
MENLO PARK, CA

FIGURE 1 FLUOROCARBON-11, CH_3CCl_3, AND CCl_4 ALONG WITH OTHER FLUOROCARBONS IN THE AMBIENT

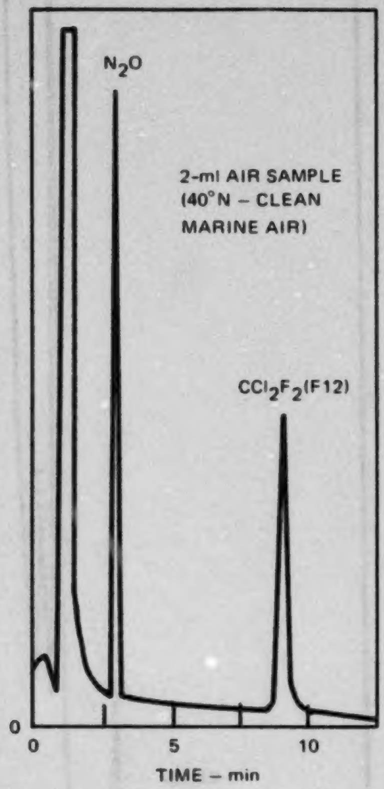


FIGURE 2 FLUOROCARBON-12, AND N_2O IN THE AMBIENT AIR

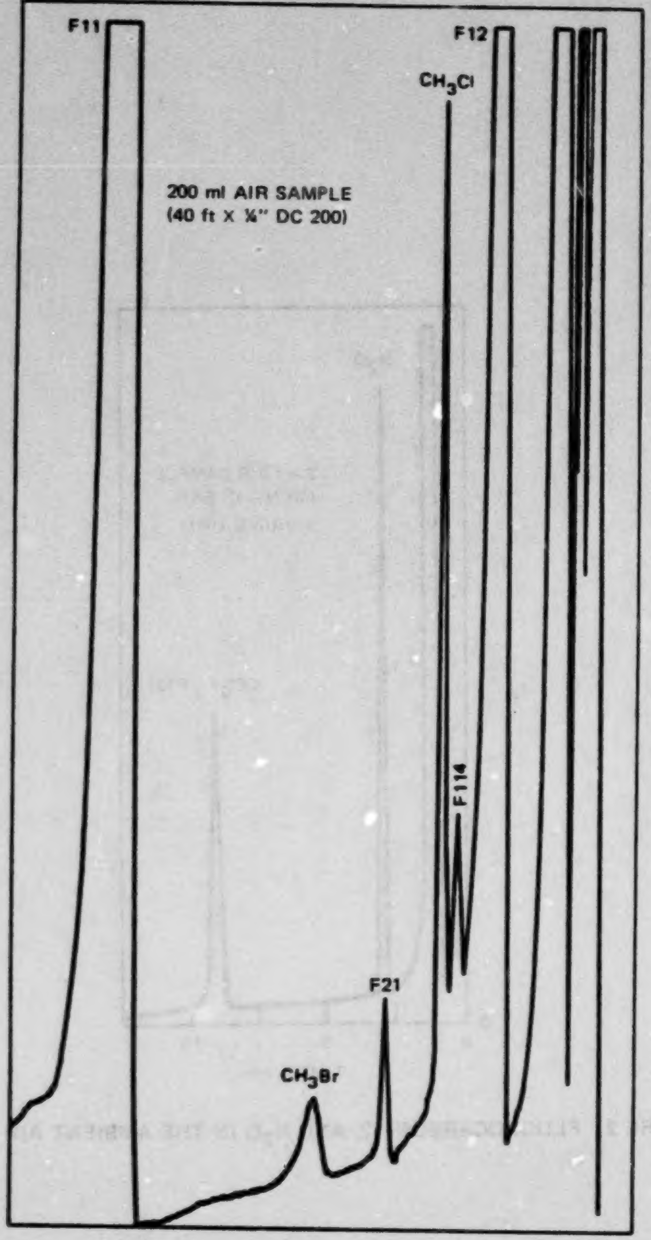


FIGURE 3 FLUOROCARBONS-12, -114, -21, -11; CH_3Cl AND CH_3Br SEPARATION FROM THE AMBIENT AIR

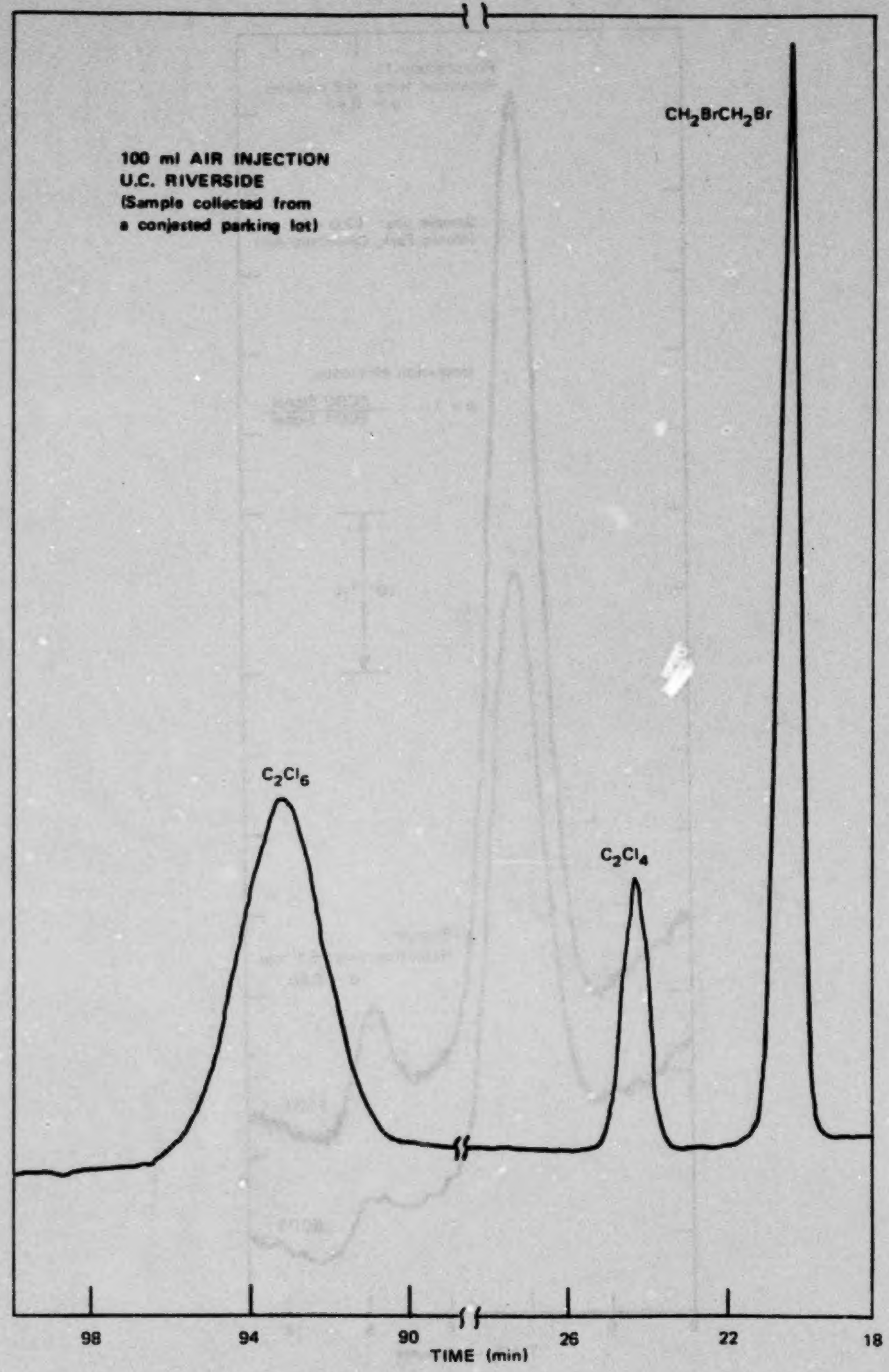


FIGURE 4 ETHYLENE DIBROMIDE AND C_2Cl_6 SEPARATION FROM AMBIENT AIR

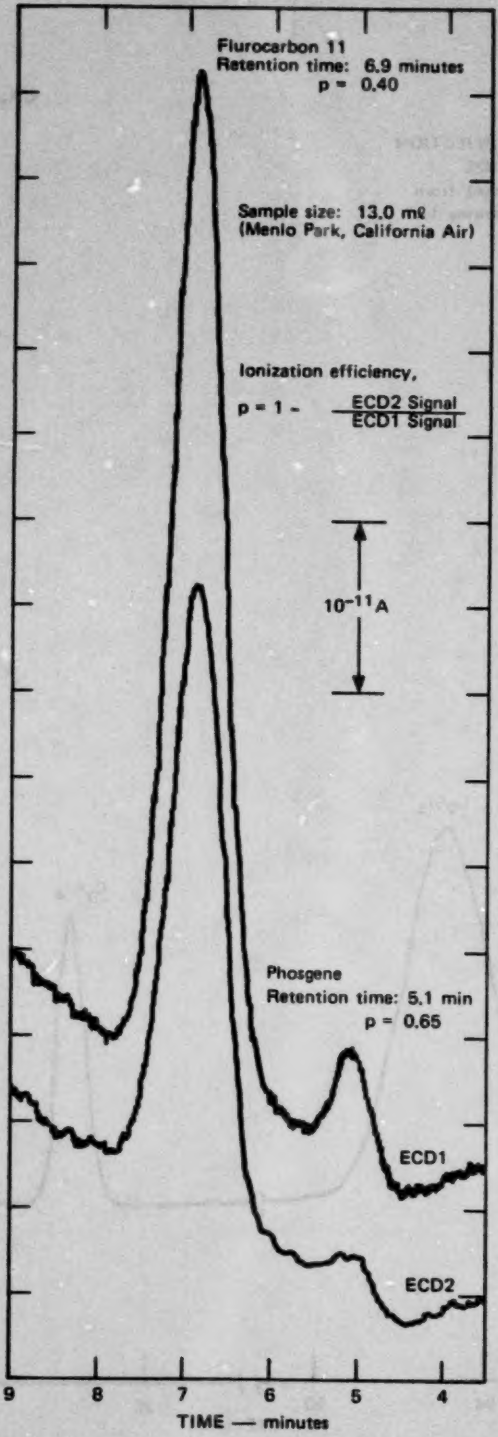


FIGURE 5 PHOSGENE SEPARATION FROM THE AMBIENT AIR

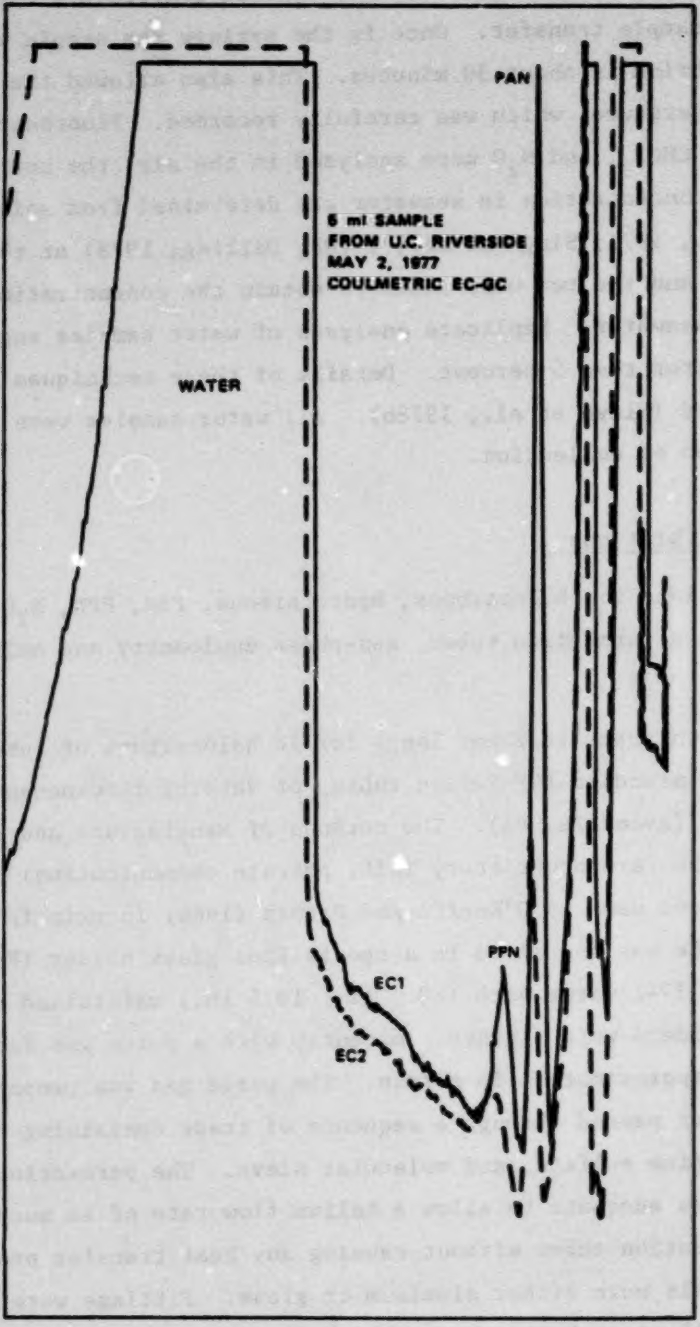


FIGURE 6 PAN AND PPN SEPARATION FROM AMBIENT AIR USING A COULOMETRIC EC-GC

of ultrapure air in an all-glass syringe of 100-ml volume. The speed with which samples were transferred ensured minimal temperature change and species loss during sample transfer. Once in the syringe the sample was allowed to reach equilibrium in about 30 minutes. This also allowed the water to reach the room temperature, which was carefully recorded. Fluorocarbons-12 and -11, CCl_4, CH_3Cl, $CHCl_3$, and N_2O were analyzed in the air, the corresponding equilibrium concentration in seawater was determined from solubility data (Junge et al., 1971; Singh et al., 1978b; Dilling, 1978) at the measured room temperature, and the two were added to obtain the concentration of the chemical in seawater. Replicate analyses of water samples suggested a precision of better than 5 percent. Details of these techniques have already been presented (Singh et al., 1978b). All water samples were analyzed within an hour or two of collection.

3. Calibrations

Calibrations for halocarbons, hydrocarbons, PAN, PPN, N_2O, and SF_6 were performed using permeation tubes, gas-phase coulometry and multiple dilutions as necessary.

Permeation tubes (3.2 in. long) for 18 halocarbons of interest, constructed from standard FEP Teflon tubing of varying thicknesses, were obtained from AID Inc. (Avondale, PA). The methods of manufacture and sealing of permeation tubes are proprietory (AID, private communication) but are very similar to those used by O'Keeffe and Ortman (1966) in principle. Each permeation tube was contained in a specialized glass holder (Figure 7) which was held in a 37-l water bath (18 × 12 × 10.5 in.) maintained at 31.0 ± 0.05°C. Permeation holders were flushed constantly with a purge gas flowing through at a rate of approximately 15 ml/min. The purge gas was prepurified helium and was further passed through a sequence of traps containing charcoal, anhydrous calcium sulfate, and molecular sieve. The permeation holder inlet coil length was adequate to allow a helium flow rate of as much as 5 l/min over the permeation tubes without causing any heat transfer problems. All tubing materials were either aluminum or glass. Fittings were either brass Swagelok or all-glass ball joints.

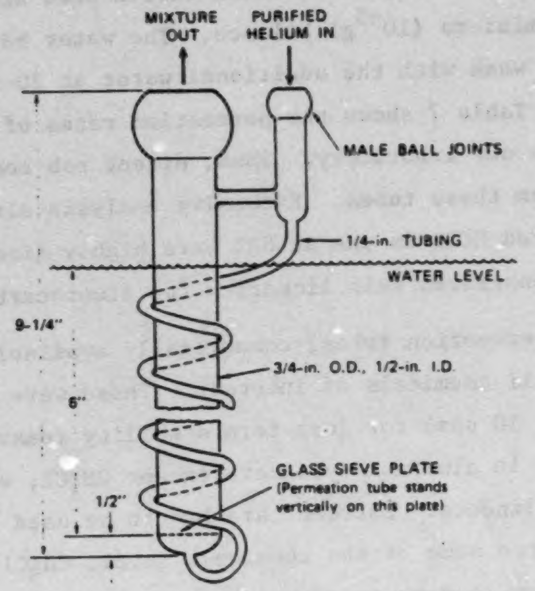

MIXTURE OUT
PURIFIED HELIUM IN
MALE BALL JOINTS
1/4-in. TUBING
WATER LEVEL
9-1/4"
3/4-in. O.D., 1/2-in. I.D.
6"
GLASS SIEVE PLATE
(Permeation tube stands vertically on this plate)
1/2"

FIGURE 7 PERMEATION TUBE HOLDER

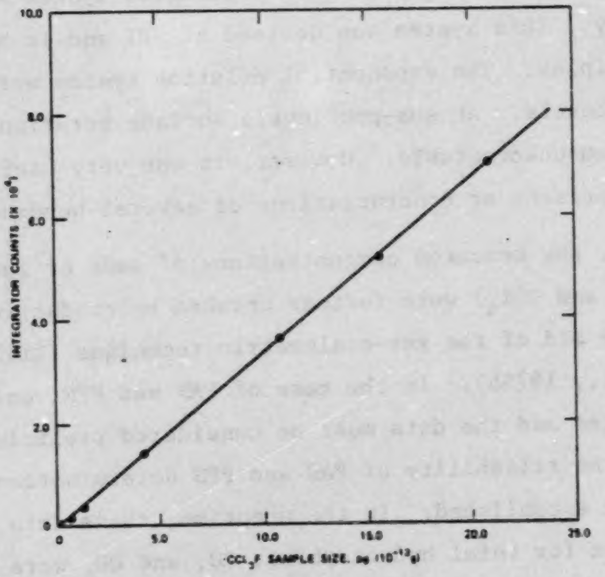


FIGURE 8 DEMONSTRATION OF LINEAR RESPONSE OF FREQUENCY-MODULATED EC DETECTOR

Permeation tubes were weighed at least once a week and in many cases twice a week on a semimicro (10^{-5}g) balance. The water bath was filled to a constant level every week with the additional water at 30-32°C to make up for evaporation losses. Table 7 shows the permeation rates of a number of chemicals measured in our laboratory. Thus, direct ppb concentration mixtures could be obtained from these tubes. Extensive analysis also suggested that the frequency-modulated ECDs in use at SRI were highly linear in the low ppb range. Figure 8 demonstrates this linearity for fluorocarbon-11.

In addition to permeation tubes, commercially available standards were obtained for nearly all chemicals of interest. These were obtained at higher concentrations (≈5 to 10 ppm) for long-term stability reasons. All of the standards were stored in aluminum cylinders except CH_3Cl, which was contained in stainless-steel cylinders. Extreme care had to be used in selecting cylinder materials since some of the chemicals (e.g., CH_3Cl) form unknown complexes with aluminum leading to potentially explosive conditions. All of the commercially available standards were rechecked with permeation tubes or our own multiple-dilution techniques. The hydrocarbon standards were checked against those available from NBS and found to agree within ±5 percent.

In addition to these, an exponential dilution system was installed in our mobile laboratory. This system was devised at SRI and is based on ultrasonic sound-wave principles. The exponential dilution system worked satisfactorily down to low ppb levels. At sub-ppb levels surface sorption problems made the use of this system unacceptable. However, it was very useful for species such as N_2O that are present at concentrations of several hundred ppb's.

In addition, the measured concentrations of some of the species (fluorocarbon-11 and CCl_4) were further checked by conducting absolute analysis with the aid of the gas-coulometric technique (Lillian and Singh 1974, Singh et al., 1975b). In the case of PAN and PPN, only gas-phase coulometry was used and the data must be considered preliminary until the confirmation of the reliability of PAN and PPN determination using gas-phase coulometry can be established. In the meantime, these data do appear reasonable. Calibration for total hydrocarbons, CO, and CH_4 were conducted in the field at least twice a day. NO_2 calibrations were conducted using a permeation tube as primary standard. Standard secondary mixtures of NO and NO_2

Table 7

PERMEATION RATE DATA FOR HALOCARBON PRIMARY STANDARDS

Compound	Tube wall thickness[*] (inch)	Permeation rate, ng/min—95% confidence limit	Mean permeation rate, ppb/l/min (25°C, 1 atm)	Status[†]	Conditioning time, weeks
CH_3Cl	0.125	1350.0 ± 80.4	653.6	S	<1
CH_2Cl_2	0.030	580.0 ± 34.2	166.8	S	<1
$CHCl_3$	0.030	132.0 ± 12.7	27.0	S	1-2
CCl_3F (F-11)	0.030	1050.0 ± 78.4	186.9	S	5-6
CH_3Br	0.030	2020.0 ± 102.2	520.2	S	1-2
CH_3I	0.030	256.6 ± 9.6	44.2	S	5-6
$COCl_2$	0.125	2460.0 ± 183.6	607.6	S	1-2
C_2H_5Cl	0.030	460.0 ± 37.8	174.4	S	1-2
CH_2CHCl	0.062	1170.0 ± 64.1	457.7	S	1-2
CH_2ClCH_2Cl	0.030	71.3 ± 6.0	17.6	S	1-2
$CHClCHCl_2$	0.030	246.0 ± 20.1	45.7	S	1-2
$CClF_2CClF_2$ (F-114)	0.030	14160.0 ± 240.0	2025.6	S	1-2
CCl_2FCClF_2 (F-113)	0.030	480.0 ± 49.6	62.6	S	5-6
CCl_2CCl_2[‡]	0.030	64.8 ± 26.1	9.5	U	...
CCl_4[§]	0.030	...	...	U	...
CH_3CCl_3[§]	0.030	...	...	U	...
CH_2BrCH_2Br[§]	0.030	...	...	U	...
CCl_2F_2 (F-12)[■]	0.125	...	...	U	...

[*] Tubes were made of FEP Teflon tubing (3.2 in. long) and were maintained at 31.0 ± 0.05°C. For tubes with wall thickness of 0.125 in., the tube o.d. was 0.375 in.; for all others the o.d. was 0.250 in.

[†] S = satisfactory; U = unsatisfactory.

[‡] There are short time periods when CCl_2CCl_2 permeation tubes perform satisfactorily; however, errors of less than 10% are difficult to obtain. TFE Teflon is expected to perform better and will be tested.

[§] Leak rate is too slow to quantify accurately and may be used as a secondary standard.

[■] Leak rate is too fast at 31°C; new permeation tube is under test.

were used in the field; O_3 primary calibrations were performed using the neutral-buffer KI method and then monitored with the Bendix O_3 calibrator.

In all field experiments, we calibrated 3 to 4 times a day by using secondary standards. These secondary standards were samples of atmospheric air that had been carefully characterized by comparing them against primary standards. Only these secondary standards were used during field operations. The frequency of use, however, was variable. For N_2O analysis, where we were aiming for a less than 1 percent precision, every analysis of an air sample was followed by the analysis of a standard.

Because of the long-term study period and the need to characterize the troposphere accurately, several air standards were retained in specially polished 5-l stainless-steel vessels. These were used to ensure long-term internal consistency. For species such as fluorocarbons-12, -11, -113, and -114, CCl_4, CH_3CCl_3, N_2O, and SF_6, they performed excellently. In most other cases, however, the trace constituents showed signs of deterioration with time. When this occurred, we had to depend largely on our ability to generate standards repeatedly.

Because halocarbons are relatively new pollutants and present at very low concentrations, the generation of primary standards is a difficult and tedious task. At the same time, the needs are such that an extremely high degree of accuracy is required. There are no agreed-upon sources of primary standards. To test the uncertainties in measurements, identical samples of air of unknown composition were analyzed by SRI and Washington State University (WSU) independently. The results of this intercomparison are shown in Table 8 and indicate reasonable agreement.

Table 8

ANALYSIS AND INTERCOMPARISON OF AN IDENTICAL AIR SAMPLE BY SRI AND WSU

Compound	Concentration	
	SRI	WSU
N_2O (ppb)	312	329
F-12 (ppt)	224	250
F-11 (ppt)	124	150
CH_3CCl_3 (ppt)	106	104
CCl_4 (ppt)	122	150

SECTION 5

EXPERIMENTAL PLAN

Our first attempt was to develop analytical methodology for a large number of species identified in Table 5. Having developed the methodology, we conducted a number of short-term field programs in urban, suburban, and clean background environments. In this chapter, we shall identify the nature of the field experiments and the mode of operation.

A. Air Sampling with the Instrumental Mobile Laboratory

All measurements over the continental United States were performed with the help of an instrumented mobile laboratory. Table 9 summarizes the equipment installed in this mobile laboratory for this program. This laboratory was air conditioned for temperature control and operated on a 220-V, 80-A circuit. Provisions were also devised to operate on 110-V input. A 200-m electrical cord was always used to station the laboratory away from the building of electrical source. The sampling manifold was all stainless steel with a variable inlet height. In almost all cases, sampling sites were chosen to have no nearby buildings that exceeded a height of 5 meters. The inlet of the sampling manifold was adjusted to be higher than nearby structures. A typical manifold inlet height was 5 m above ground.

We conducted a total of 14 field studies in the western half of the United States with the help of the mobile laboratory. The site locations are shown in Figure 9. Table 10 provides additional information on the nature of the sites selected. A wide variety of sites and locations was considered. The Pacific Coast provided an ideal location for clean background conditions because of westerly winds and virtually no source within several thousand miles upwind. Occasionally, however, the winds were easterly and urban effects were encountered. Since some of the species being measured in this study are excellent indicators of urban contamination, such data are not considered in determining the geochemical background of pollutant levels.

Table 9

ENVIRONMENTAL MOBILE LABORATORY INSTRUMENTATION

Instrumentation	Feature	Analysis
Perkin Elmer 3920 GC1	2 ECD* and 1 dual FID†	Trace constituents
Perkin Elmer 3920 GC2	2 ECD and 1 dual ECD	Trace constituents
Perkin Elmer 3920 GC3	2 ECD and 1 dual ECD	Trace constituents
Coulometric dual EC-GC	Coulometric ECD	Halocarbons, PAN, PPN, $COC\ell_2$ analysis and calibration
Beckman 6800	FID	$CO-CH_4-THC$
Horiba AIA-24	NDIR‡	CO, CO_2
Bendix 8101-B	Chemiluminescent	NO, NO_2
Dasibi Model 1003 AH	Photometric principle	Ozone
AID Model 560	Chemiluminescent	Ozone
Monitor Labs Model 8440E	Chemiluminescent	NO and NO_x
Bendix 8002	Chemiluminescent	O_3
Eppley Pyranometer		Solar flux
Eppley UV Radiometer		Ultraviolet radiative flux
Meteorological equipment		Wind speed, wind direction, temp, pressure, dew point, relative humidity, etc.
Auto Lab IV data System (No. 1)		All gas chromatography data input
Digitem data system (No. 2)		All continuous air quality and meteorological data
Stainless steel manifold		Sampling of HCs, halocarbons, etc.
Teflon manifold		Sampling of O_3, NO, NO_x

*Electron capture detector.

†Flame ionization detector.

‡Nondispersive infrared.

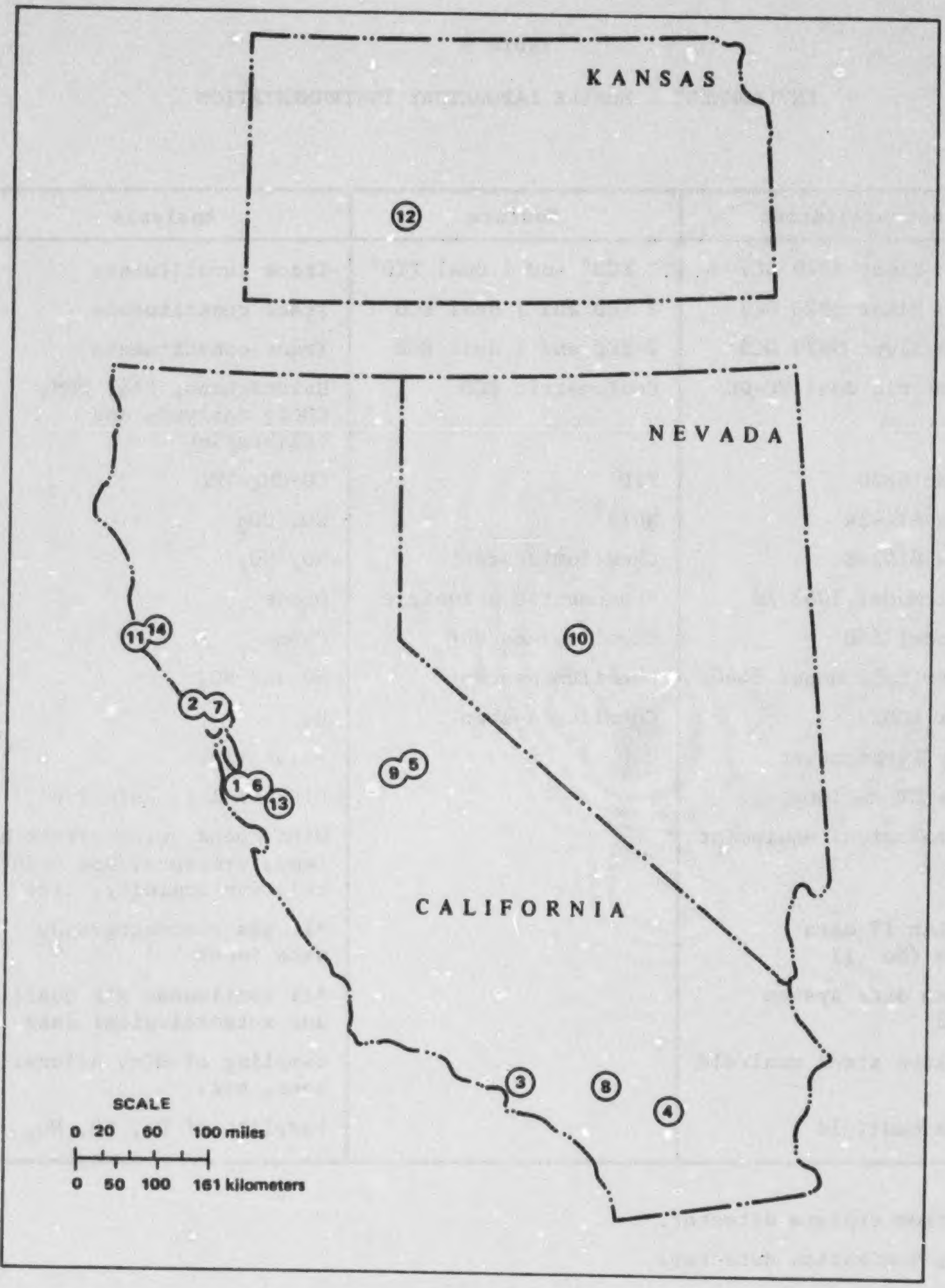

KANSAS
12
NEVADA
10
11
14
2
7
9
5
1
6
13
CALIFORNIA
3
8
4
SCALE
0 20 60 100 miles
0 50 100 161 kilometers

FIGURE 9 LOCATION OF MONITORING SITES ON THE CONTINENTAL UNITED STATES

Table 10

MEASUREMENT SITES OVER THE CONTINENTAL UNITED STATES

Site No.	Location Name	Lat. (°N)	Long. (°W)	Approximate Elevation MSL, meters	Monitoring Period	Nature of Site
1	Stanford Hills, CA	37° 23'	122° 14'	120	11/23 - 11/30, 1975	Clean site subject to urban transport
2	Point Reyes, CA	38° 07'	122° 56'	10	12/01 - 12/12, 1975	Clean marine
3	Los Angeles, CA	34° 04'	118° 11'	20	4/28 - 5/04, 1976	Urban
4	Palm Springs, CA	33° 48'	116° 33'	800	5/05 - 5/11, 1976	Urban-suburban
5	Yosemite, CA	37° 39'	119° 40'	2380	5/12 - 5/18, 1976	Remote-high altitude
6	Menlo Park, CA	37° 24'	122° 12'	20	5/24 - 5/28, 1976	Suburban
7	Mill Valley, CA	37° 59'	122° 39'	760	1/11 - 1/27, 1977	Clean marine-subject to urban transport
8	Riverside, CA	33° 54'	117° 23'	250	4/25 - 5/04, 1977	Urban-suburban
9	Badger Pass, CA	37° 39'	119° 42'	2380	5/05 - 5/13, 1977	Remote-high altitude
10	Reese River, NA	38° 59'	117° 28'	1982	5/14 - 5/20, 1977	Remote-high altitude
11	Point Arena, CA	38° 57'	112° 44'	10	5/23 - 5/30, 1977	Clean-marine
12	Jetmore, KA	37° 59'	99° 53'	850	6/01 - 6/07, 1978	Remote continental
13	San Jose, CA	37° 20'	121° 53'	20	8/21 - 8/27, 1978	Urban
14	Point Arena, CA	38° 57'	123° 44'	10	8/30 - 9/05, 1978	Clean marine

During each of the field studies, the mobile laboratory was installed in a carefully selected place and measurements were conducted for a period of one to two weeks. Despite the difficulty in logistics, we decided that 24 h operation is necessary for proper characterization of the atmosphere. Therefore, in all cases a round-the-clock measurement schedule was followed.

B. Global Sampling

The global atmospheric measurements extended from 64°N to 90°S latitudes. The Pacific Ocean water measurements were conducted between 46°N to 40°S latitudes. Figure 10 describes the sampling locations of the four experiments. In all the global experiments it was our objective to obtain the cleanest possible samples that would be representative of background conditions. The global sampling and analysis program was composed of four experiments. Three of these involved air analysis and the fourth one involved water analysis.

1. Air Sampling

a. Whole-Air Batch Sampling

All batch sampling was conducted in specially designed stainless steel and glass vessels of 1 liter volume each. Both types of sampling vessels were so designed that they could be easily pressurized to 40 psi. Figures 11 and 12 show these sampling vessels. The stainless-steel sampling vessels were electrochemically polished to have an inert surface and were commercially obtained from D and F Instruments. The glass vessels were constructed at SRI International. Prior to use, they were heated to 250°C and flushed with ultrapure helium that was cryogenically cleaned. A hundred volumes of the sampling vessel were exchanged over 100 minutes (helium flow rate ≃1 liter/minute). The sampling vessels were then checked for background contamination, and the procedure was repeated until the background contamination of the sampling vessels was reduced to less than 2 to 3 percent of the expected background concentration of a given trace constituent. The sampling vessels were also placed in a contaminated room and rechecked for pressure stability and background contamination. Typically, the vessels that maintained the pressure were not affected by room contamination because of the high positive pressure maintained in these vessels.

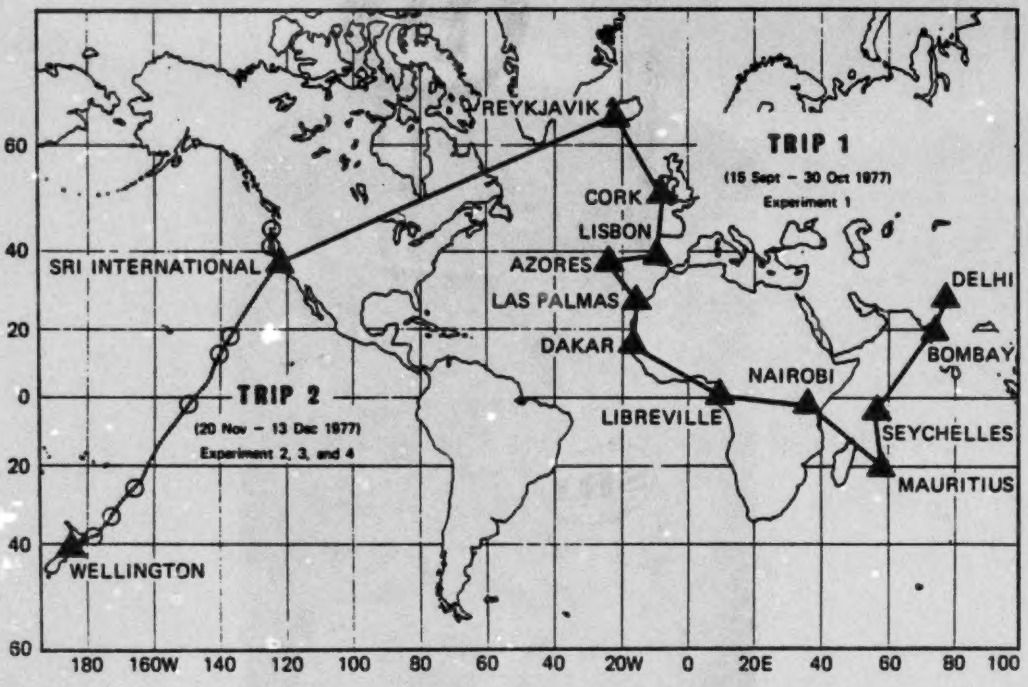

REYKJAVIK
TRIP 1
(15 Sept – 30 Oct 1977)
Experiment 1
CORK
LISBON
AZORES
LAS PALMAS
DAKAR
DELHI
BOMBAY
NAIROBI
LIBREVILLE
SEYCHELLES
MAURITIUS
SRI INTERNATIONAL
TRIP 2
(20 Nov – 13 Dec 1977)
Experiment 2, 3, and 4
WELLINGTON
60
40
20
0
20
40
60
180
160W
140
120
100
80
60
40
20W
0
20E
40
60
80
100

FIGURE 10 MAP SHOWING THE SAMPLING LOCATIONS FOR THE FOUR EXPERIMENTS

The open circles indicate the deep seawater (0 to 300 m) sampling sites.

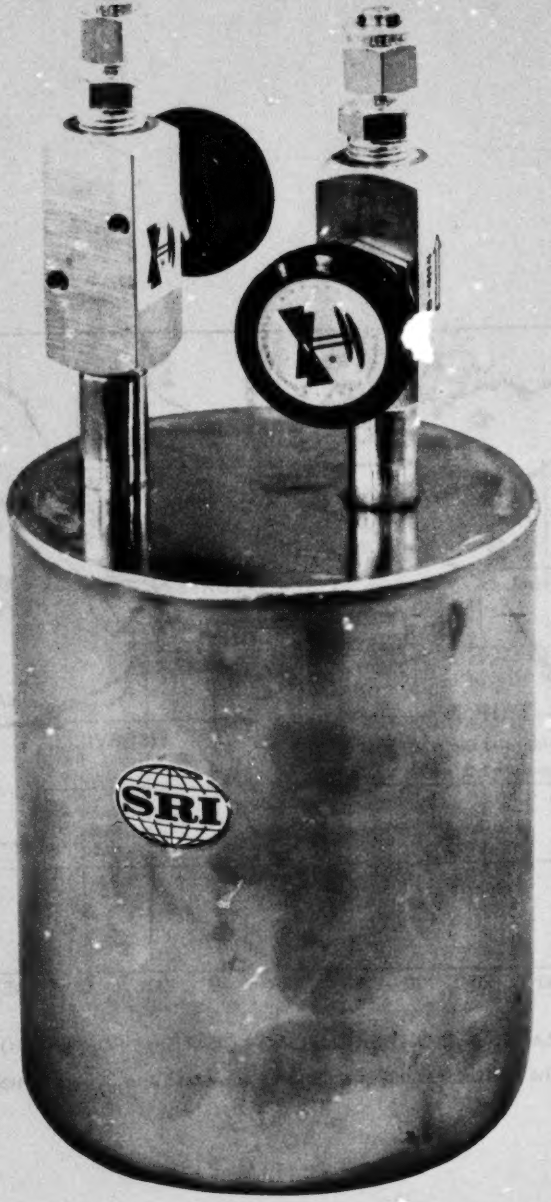


FIGURE 11 SPECIALLY TREATED 1-LITER STAINLESS-STEEL SAMPLING VESSEL FOR COLLECTING GRAB SAMPLES

FIGURE 12 ONE-LITER GLASS SAMPLING VESSEL

Prior to air sampling, the sampling vessels were carried at a positive pressure of helium (≈5 psi) to prevent any contamination en route. During sampling each vessel was flushed with 100 to 150 liters of ambient air and then pressurized to 40 psi with a special stainless-steel Metal Bellows compressor pump (Model MB 158), which could maintain a continuous flow rate of 25 liters/minute. A 200-m electrical cord was carried so we could sample away from the source of electricity, usually a farmhouse or an abandoned building near the ocean. Two blank samples were also carried to ensure that no contamination occurred during sample collection and analysis.

Experiment 1--Pressurized air samples were collected between 64°N and 20°S in specially treated 1-liter stainless-steel and glass vessels. The sampling vessel and the sampling procedure are discussed in detail below. Typically, four samples--two with glass and two with stainless-steel vessels--were collected at each site. Figure 10 shows the locations from which air was collected (Trip 1). The air samples were always collected at the cleanest possible locations under the most favorable meteorological conditions. A few urban samples were also collected. Trip 1 sampling continued from 15 September to 26 October 1977. These samples were analyzed after 26 October 1977.

Experiment 2--Air samples were collected on board the U.S. Coast Guard icebreaker, Burton Island, which traveled from Oakland, California to Wellington, New Zealand, covering 36°N to 42°S latitude between 120°W and 175°E longitude. The actual itinerary is shown in Figure 10 (Trip 2). Air samples were collected in stainless-steel vessels, as in Experiment 1. This experiment was conducted from 20 November to 13 December 1977, and these samples were later analyzed at our laboratories in Menlo Park, California.

b. In Situ Sampling

Experiment 3--This experiment was conducted during the same oceanographic cruise and at the same time as Experiment 2. The major difference in Experiment 3, however, is that the air samples were analyzed in situ with two 3920 Perkin Elmer gas chromatographs, each equipped with two electron-capture detectors and one flame-ionization detector, and a coulometric gas chromatograph that were installed on board.

Aboard the Burton Island, in situ air sampling was conducted using a stainless-steel manifold with two inlet positions. We hoped that contamination from the ship exhaust could be avoided by switching from one manifold inlet to the other if meteorological conditions turned unfavorable. Both manifold inlets were at the front of the vessel, about 10 m above sea level and 20 m apart. At any given moment, only the manifold inlet that would obtain the cleanest possible air was operational. The decision to select the right manifold inlet was made on the basis of wind data. On extremely calm days (wind speed <5mph) it was impossible to avoid exhaust contamination from either of the sampling manifolds, and air samples were collected in glass syringes from the best possible location. If clean air samples could not be obtained, analysis of air samples was terminated. Because the Burton Island is round-bottomed and rolls excessively, we could not monitor on highly stormy days.

2. Water Sampling

Experiment 4--The task of water sampling from depths of 0 to 300 m was handled by the Burton Island crew. Paired samples were obtained from 0 to 300 m at 50-m intervals. Water temperature at these depths was also measured. Each water sample provided 0.5 liters of seawater and was usually analyzed within an hour or two of collection. Figure 13 shows the water sampling being conducted.

Water samples from the Pacific Ocean were analyzed on-site aboard the Burton Island (Trip 2). In addition, water samples from 40°N to 46°N in the Pacific Ocean were also analyzed. Seawater samples were collected from the surface (0 to 2 m) and from depths of 0 to 300 m at intervals of 50 m. Analysis of water samples was limited to six key species. These were N_2O, CH_3Cl, CCl_2F_2, $CHCl_3$, CCl_3F and CCl_4. One CCl_3F and CCl_4 paired surface sample a day was collected during Trip 2. The deep-water sampling sites are identified in Figure 10.

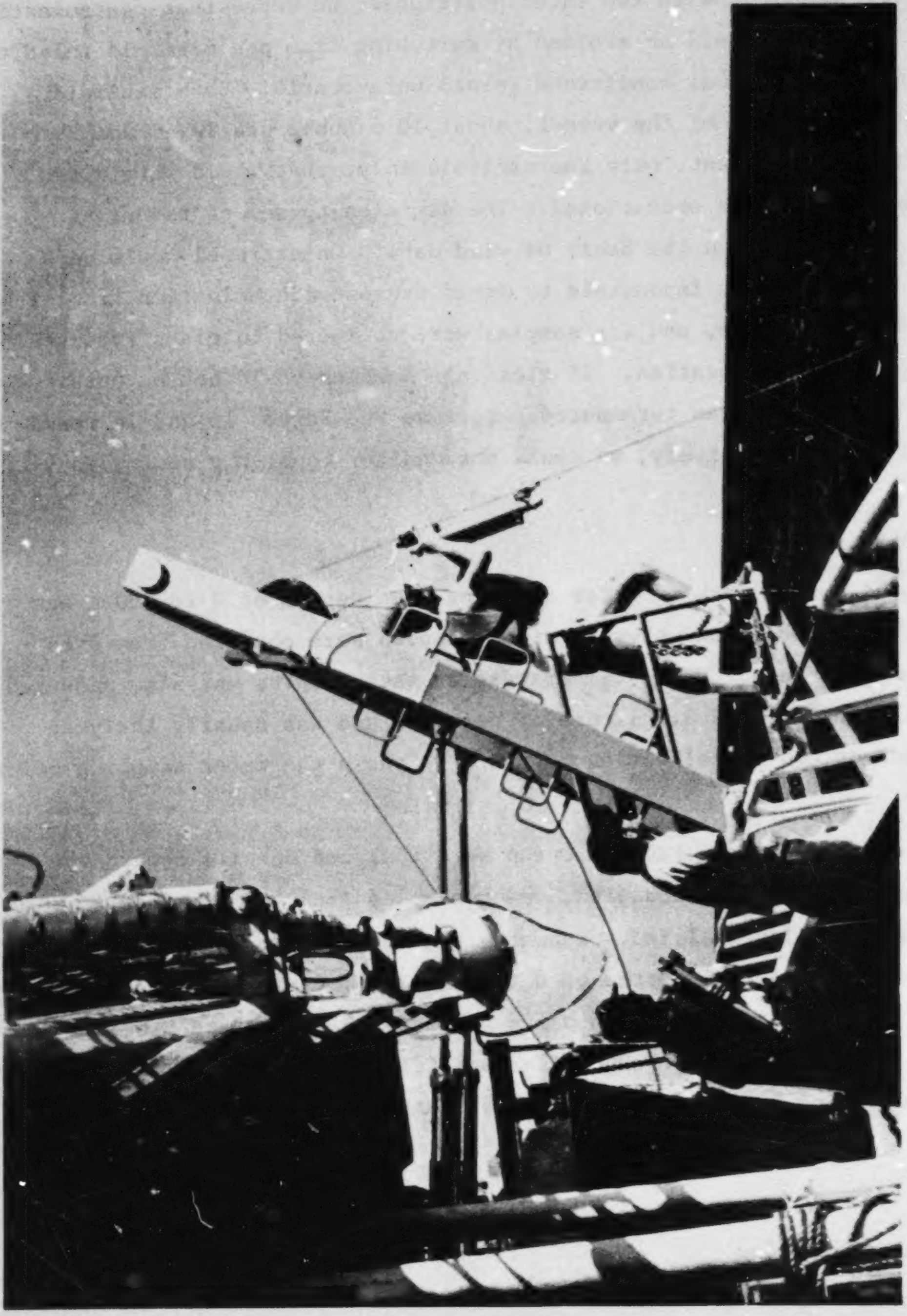


FIGURE 13 DEEPWATER SAMPLING IN THE PACIFIC OCEAN

SECTION 6

DISTRIBUTION, SOURCES, AND SINKS OF NITROUS OXIDE

Nitrous oxide (N_2O) has received attention from atmospheric scientists in recent years because of the hypothesis that continued use of nitrogen fertilizers can increase the atmospheric abundance of N_2O, thereby causing a depletion in the stratospheric ozone (McElroy et al., 1976; Crutzen, 1976; Liu et al., 1977). Estimates of the depletion of stratospheric ozone by N_2O are dependent on two important factors: the residence time of N_2O in the atmosphere and the nature of its sources. Stratospheric ozone depletion estimates increase when the residence time is longer (Johnston, 1977), and when soil is a major source of N_2O (McElroy et al., 1976). The atmospheric residence time of N_2O is unknown, and widely varying estimates of 2 to 150 years have been suggested. Reliable long-term N_2O atmospheric data are currently unavailable, and no agreement exists on whether the N_2O atmospheric levels have been steadily increasing, decreasing, or have remained unchanged (Ellsaesser, 1977). Both the ocean and the soil have been identified as possible sources of N_2O, but their net contribution to the atmospheric burden of N_2O is a matter of considerable uncertainty. Oceans, for example, have been considered both significant sources of N_2O (Hahn, 1974) and net sinks (McElroy et al., 1976). In this study we provided global measurements of N_2O in the atmosphere and the Pacific Ocean and complemented these with several short-term field experiments conducted over the past 3 years in the western United States.

A. Atmospheric N_2O Measurements

N_2O measurements in the western United States were conducted with the help of a mobile laboratory. The global samples were collected in specially treated stainless-steel and glass sampling vessels. The sampling and analysis details for N_2O have already been provided in sections IV and V.

Figure 14 shows the global distribution of N_2O from data obtained in November-December of 1977. The Northern Hemisphere average background concentration of 311 ± 2.3 ppb (ppb = 10^{-9} v/v), the Southern Hemisphere average background concentration of 311 ± 2.8 ppb, and the global average of 311 ± 2.6 ppb are scarcely different from one another. Thus, it appears that N_2O is very uniformly distributed, and the standard deviation of the global variability is 0.8% (σ_t). Because part of this variability is due to the precision of our measurements (σ_p = 0.4%) and to the small variability of about 0.2% (σ_{RH}) associated with the RH corrections, a net atmospheric variability of 0.7% (σ_a) can be calculated ($\sigma_a^2 = \sigma_t^2 - \sigma_p^2 - \sigma_{RH}^2$). Using the approximate statistical derivation of Junge (1974), an atmospheric residence time of 20 years ($\tau_{N_2O} = \frac{14}{\sigma a}$) can be calculated.

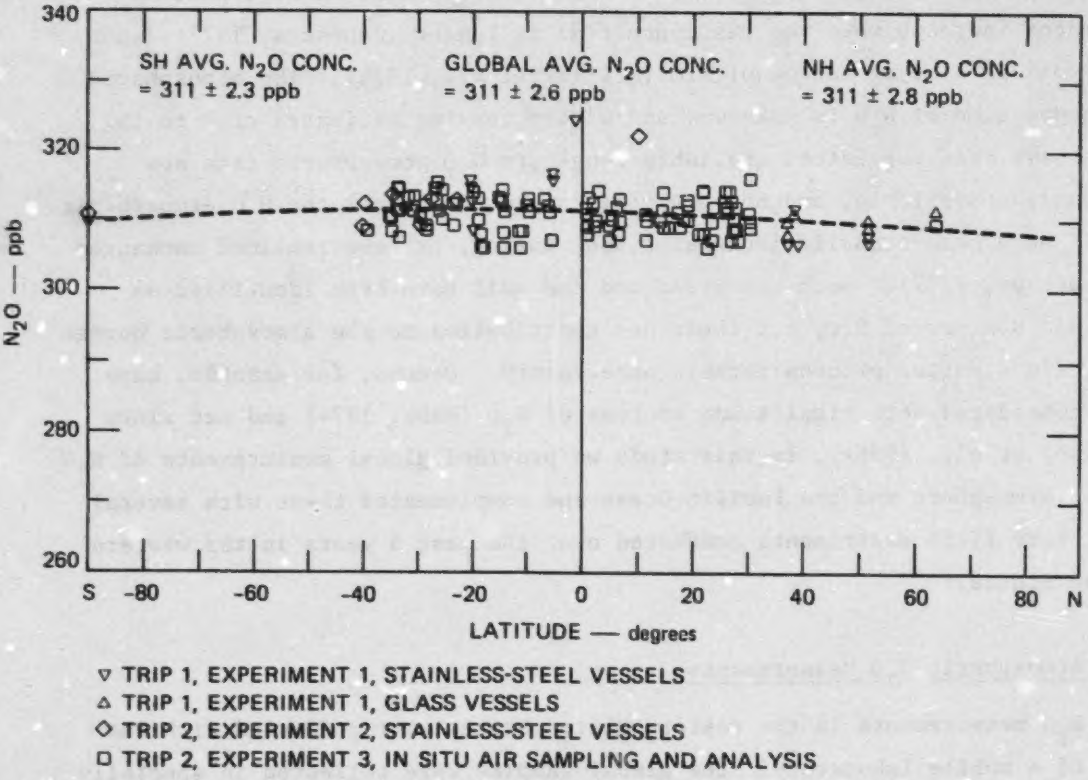


FIGURE 14 GLOBAL DISTRIBUTION OF N_2O

We have been conducting N_2O measurements since 1975, and have also retained air samples since September 1975. In the interim, we have conducted a number of short-term studies to measure N_2O background in various seasons on the West Coast of the United States. Our measurements between November 1975 and August 1978 (Figure 15) show no systematic average increase in N_2O. However, the precision of our early measurements was not very high because of infrequent calibrations (Figure 15). To alleviate this deficiency we carried the air samples we collected in September 1975 and compared them with in situ air samples between 24°N and 35°S on Trip 2 (November, 1977). Table 11 shows a comparison of replicate analysis of air samples from 1975 and 1977. The average N_2O concentration of air samples from 1975 was found to be 312.3 ± 0.81 ppb; in the in situ samples of November-December 1977 it was 311.8 ± 1.14 ppb. These averages are statistically indistinguishable. It thus appears that any change in that atmospheric abundance of N_2O since 1975 has been well within the atmospheric variabilities of N_2O.

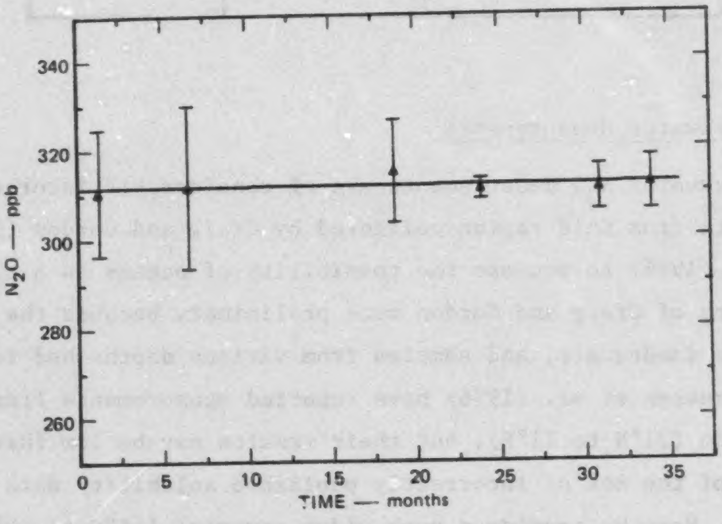


FIGURE 15 ATMOSPHERIC GROWTH OF N_2O WITH TIME

Time period beginning 1 November 1975

Table 11

AMBIENT N_2O CONCENTRATIONS (ppb) IN 1975 AND 1977

Latitude	September 1975	November-December 1977
24°N	312	310
18°N	311	312
14°N	313	313
4°N	312	311
1°N	313	312
4°S	313	312
15°S	313	313
25°S	312	310
30°S	313	313
35°S	311	312
Average concentration (±σ)	312.3 ± 0.81	311.8 ± 1.14

B. Pacific Seawater Measurements

Pacific seawater N_2O measurements are of considerable interest because preliminary data from this region collected by Craig and Gordon (1963) led McElroy et al. (1976) to propose the possibility of oceans as a sink for N_2O. The Pacific data of Craig and Gordon were preliminary because the measurement sensitivity was inadequate, and samples from various depths had to be lumped together. Rasmussen et al. (1976) have reported measurements from the eastern tropical Pacific (31°N to 11°S), but their results may be low (Hahn and Junge, 1977) because of the use of incorrectly published solubility data (Junge et al., 1971). Here we provide a much wider coverage (46°N to 40°S) of N_2O data from the North and South Pacific. To the extent that the Pacific Ocean is representative of world oceans in terms of microbial activity (McElroy et al., 1976), our data tend to remedy some of the past deficiencies in available oceanic N_2O data.

Replicate seawater samples from the Pacific Ocean from 45°N to 40°S were analyzed during Trip 2. Sampling locations and the sampling and analysis methodology have already been discussed in Section IV. A total of 16 paired surface seawater samples (0 to 2 m) were analyzed. In eight instances, N_2O analyses were conducted down to 300-m depth at 50 m intervals (see Figure 10). In a majority of cases, replicate samples indicated concentration differences that were within 5 percent. Occasionally a greater difference of 15 percent was encountered. In all cases the concentrations were averaged. There were also some instances when only a single sample could be analyzed. Such situations occurred largely because of unfavorable weather conditions resulting in unsafe working conditions. The variation of surface seawater N_2O concentrations, percentage supersaturation, and seawater temperature with latitude is shown in Table 12 and plotted in Figure 16. It is clear from Figure 16 that in all instances an N_2O supersaturation was observed. The average surface N_2O concentration was found to be 0.38 μg/l and the average surface saturation was 133 percent, with a maximum of 190 percent near the equator (Table 12).

From the surface N_2O data it is possible to calculate the flux, F, of N_2O into the atmosphere by using a simple film diffusion model:

$$F = \frac{D(T)}{Z} (C^w - C^w_{eq}) \qquad (1)$$

where D(T) is the film diffusion coefficient for N_2O in water and is a function of temperature; Z is the stagnant film depth (Broecker and Peng, 1974) which has been measured to be 60 ± 30 μm (μm = 10^{-6}m) for the world ocean; C^w is the concentration of N_2O in water; and C^w_{eq} is the N_2O concentration in equilibrium with the atmospheric abundance of N_2O.

For our calculations we have selected Z = 60 m and used the solubility data presented in Singh et al. (1978b). The variation of D(T) with temperature was obtained from Broecker and Peng (1974). Our choice of Z is the one recommended by Hahn and Junge (1977), but the actual value of Z may be higher than 60 μm for a biologically active gas such as N_2O. The mean N_2O concentration in the atmosphere was taken to be 311 ppb. The variation of calculated flux with latitude is also shown in Table 12 and Figure 16. An average N_2O flux of 36 x 10^{-14} g/cm^2/s was calculated. Table 13 shows the N_2O data

Table 12

N_2O CONCENTRATION IN PACIFIC SURFACE WATER*

Date	Lat	Long	Surface Water Temp (C°)	N_2O Concentration (μg/1)	N_2O Saturation	Flux† x 10^{-12} (g/cm^2 s)
10-29-76	45°35'N	125°55'W	13.5	0.46	115	0.173
10-28-76	41°35'N	125°35'W	14.2	0.46	120	0.224
11-25-77	19°02'N	137°48'W	24.3	0.36	133	0.347
11-26-77	15°43'N	140°05'W	25.5	0.35	130	0.323
11-27-77	11°52'N	142°05'W	25.4	0.41	152	0.561
11-28-77	06°35'N	145°14'W	28.4	0.31	124	0.258
11-29-77	02°40'N	147°43'W	26.5	0.37	141	0.438
11-30-77	01°26'S	150°10'W	27.6	0.48	190	0.955
12-01-77	06°07'S	153°13'W	28.1	0.31	125	0.264
12-02-77	09°07'S	155°35'W	28.8	0.31	124	0.261
12-04-77	18°24'S	161°42'W	26.7	0.46	175	0.808
12-05-77	22°38'S	164°26'W	24.8	0.34	128	0.291
12-06-77	25°40'S	167°33'W	23.2	0.36	124	0.261
12-07-77	30°14'S	171°18'W	21.5	0.35	115	0.164
12-08-77	33°40'S	170°50'W	18.5	0.40	119	0.211
12-11-77	39°05'S	179°13'W	16.9	0.42	118	0.204
Average				0.38	133	0.359

*Water from 0 to 2 meters.

†Flux calculation assumes a stagnant film thickness of 60 μm.

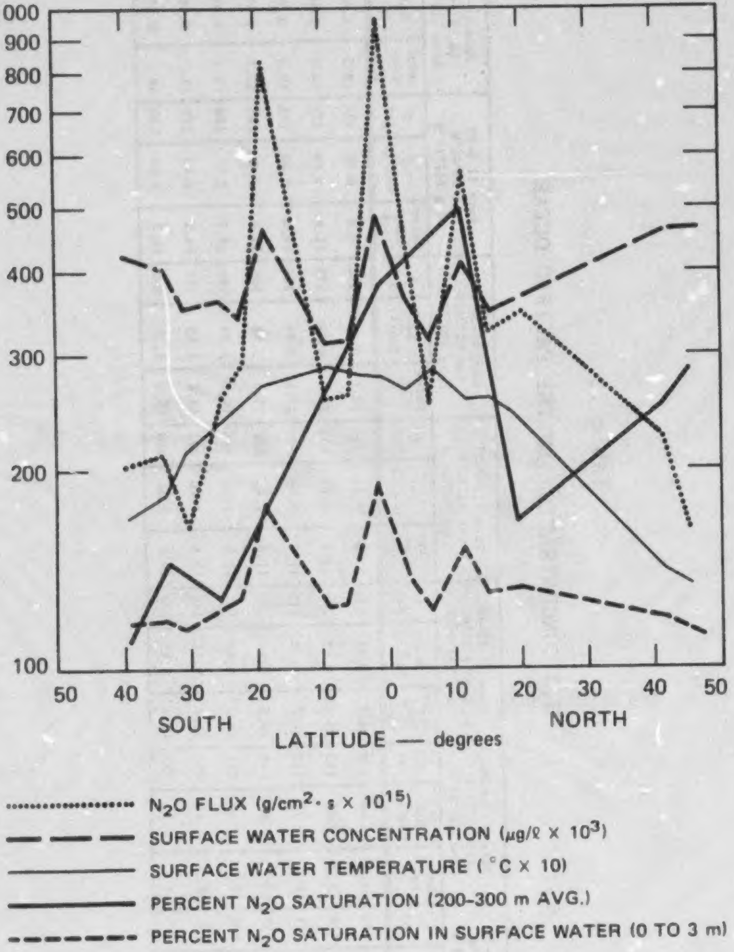


FIGURE 16 N_2O SUPERSATURATION IN THE PACIFIC OCEAN (46°N-40°S)

Table 13

N_2O CONCENTRATION IN THE PACIFIC OCEAN

Depth (m)	Date 10-29-76 Lat 45°35'N Long 125°55'W			Date 10-28-76 Lat 41°35'N Long 125°55'W			Date 11-25-77 Lat 19°02'N Long 137°48'W			Date 11-27-77 Lat 11°52'S Long 142°05'W			Date 11-30-77 Lat 01°26'S Long 150°10'W			Date 12-6-77 Lat 25°40'W Long 167°33'W			Date 12-8-77 Lat 33°40'S Long 170°50'W			Date 12-11-77 Lat 39°05'S Long 179°13'W		
	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat	Water Temp (°C)	N_2O (μg/l)	% Sat
0	13.5	0.46	115	14.2	0.46	120	24.3	0.36	133	25.4	0.41	152	27.6	0.48	190	23.2	0.36	124	18.5	0.40	119	16.9	0.42	118
50	12.2	0.56	136	13.2	0.58	145	24.0	0.78	289	17.4	0.83	237	27.5	0.34	135	21.8	0.40	133	14.6	0.44	144	16.8	0.47	132
100	10.5	0.73	166	12.0	0.71	169	24.0	0.58	215	12.2	2.48	605	27.5	0.39	154	19.4	0.40	123	13.5	0.50	125	14.7	0.43	113
150	9.6	0.95	213	10.7	0.96	218	20.6	0.42	133	11.8	2.83	690	25.8	0.40	149	18.5	0.48	143	12.7	0.58	141	13.7	0.47	119
200	9.0	1.27	270	10.0	1.08	237	19.2	0.40	121	11.1	2.09	486	19.0	0.93	282	17.7	0.42	120	12.2	0.59	144	13.4	0.47	118
250	8.6	1.37	291	9.5	1.16	252	17.3	0.51	146	10.6	2.10	477	13.6	2.08	527	16.3	0.46	127	11.7	0.58	141	13.1	0.45	113
300	8.2	1.42	296	9.2	1.18	257	12.4	0.93	227	10.2	2.31	519	13.4	1.35	342	15.2	0.49	130	10.7	0.65	148	13.0	0.41	103

between 0 and 300 m in the Pacific Ocean at 50-m intervals. These data are plotted in Figure 5. It is clear from Figure 17 that the maximum N_2O concentration below the top mixed layer was 1 to 7 times the surface N_2O concentration. The most intensive synthesis of N_2O was near the equator. Near the southern midlatitudes, the supersaturation was found to be marginal. The average variability of N_2O saturation between 200- and 300-m depth with latitude is also shown in Figure 16.

C. Results and Discussion

The atmospheric distribution of N_2O was found to be uniform around the globe with an average global concentration of 311 ppb. A number of investigators have recently reported N_2O concentrations that vary from 290 to 330 ppb, and have been summarized by Liu et al. (1977). This is largely because of the unavailability of primary standards at this time. A ±6 percent uncertainty in the absolute concentration of N_2O currently exists. Some of this uncertainty (between 0 to 2 percent) can be attributed to the manner of reporting data. We have reported our data at 50 percent relative humidity and 25°C while some have reported data at 0 percent relative humidity and yet others have made no relative humidity correction (Rasmussen et al., 1976). However, the most important aspects of atmospheric measurements rest on the variability of relative concentrations of N_2O rather than its absolute value.

The small atmospheric variability of N_2O ($\sigma_a = 0.7\%$) suggests a τ_{N_2O} of greater than 20 years. The τ_{N_2O} is higher than 20 for two major reasons:

- All our data were collected within 15 m of sea level and can be expected to show a larger σ_a because of the close proximity of the oceanic source.
- The atmospheric variabilities are approaching the precision of the analysis and the true σ_a is probably less than 0.7 percent.

In our opinion, the past estimates of τ_{N_2O} of 2 to 10 years (Hahn and Junge, 1977) were derived from measurements of less precision, which result in the calculation of a large σ_a and a short τ_{N_2O}.

Our data, collected over a period of about 3 years, while limited, suggest an unchanging background of N_2O. There appears little doubt that during this period (1975 to 1978) the change in N_2O concentrations has been less than the

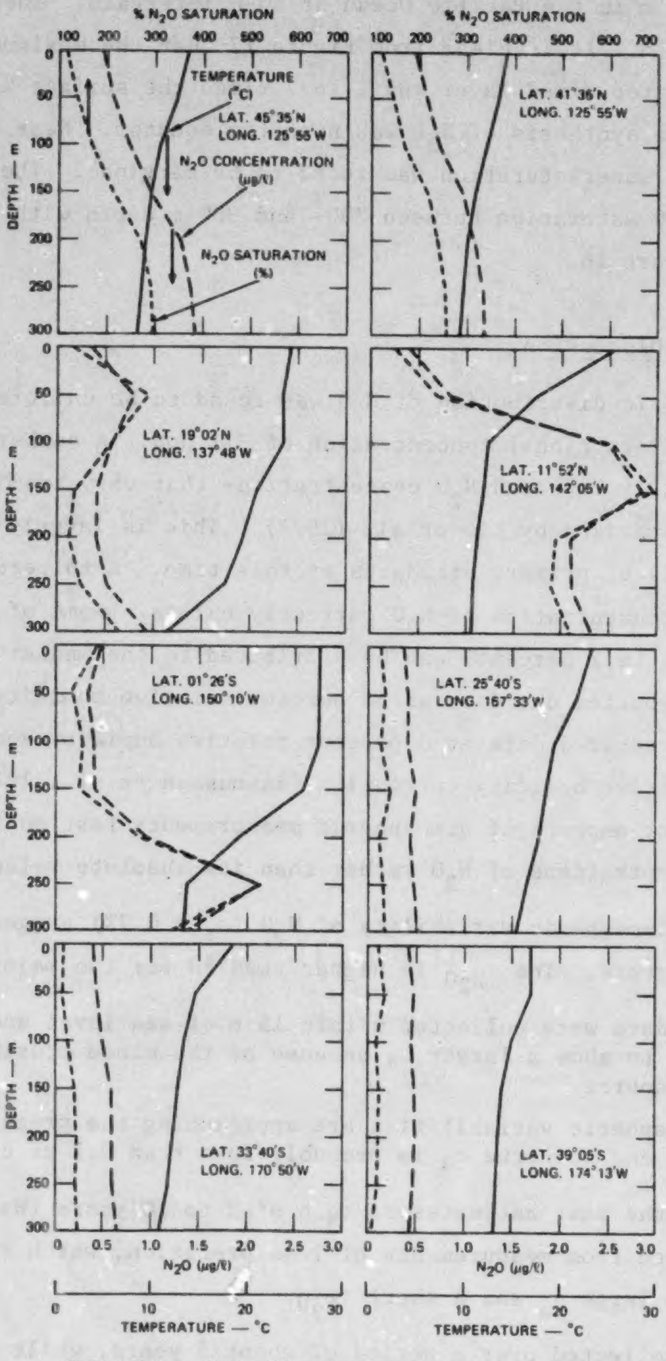


FIGURE 17 DISTRIBUTION OF N$_2$O IN THE PACIFIC

atmospheric variability of N_2O. This is in disagreement with the upper limit of a 4 percent projected increase in N_2O abundance during this time because of nitrogen fertilizer applications (Crutzen, 1976). It thus appears that the lower limits of projected N_2O increases, which suggest essentially no change during this period, are more likely to be reliable (Crutzen, 1976; Hahn and Junge, 1977).

Based on our measurements in the Pacific, we obtained an average N_2O flux of $36 \times 10^{-14}\ \mathrm{g/cm^2/s}$ and an average saturation of surface water of 133 percent. Hahn (1974) reported a saturation of 123 percent in the Atlantic between 38°N and 50°N. This can be compared with a 118 percent saturation measured by us between 41°N and 46°N. Comparison of data between the Pacific and Atlantic (Hahn, 1974) would suggest that our measured N_2O saturation of 133 percent is reasonably representative of global waters between 45°N and 45°S. Additional data are required to make this generalization, but based on currently available information this assumption does not seem to be unreasonable. In the rest of the world ocean body we assume an average saturation of 115 percent based on Hahn's measurements. Using the average 133 percent saturation for the 74 percent of the seawater between 45°N and 45°S, and 115 percent for the remaining ocean surface, a net N_2O exchange of 30 million tons (N_2O)/year can be calculated. This estimate of oceanic N_2O flux is less than half of the best estimates of 70 million tons (N_2O)/year derived by Hahn and Junge (1977).

We wish to further add that this flux estimate is critically dependent on the film thickness used in the film model. While we have used a film thickness of 60 μm for comparative purposes (Hahn and Junge, 1977), the possibility that this film thickness could be as high as 90 μm cannot be ruled out. Therefore, our estimated oceanic flux would be between 20 and 30 million tons (N_2O)/year (or 13 and 19 million tons (N)/year). This source alone allows a turnover time of 75 to 110 years for atmospheric N_2O. Despite the uncertainties, our findings support the conclusion that oceans are most likely a net source of N_2O. This is in agreement with the findings of Junge et al. (1971) and Hahn (1974) but in disagreement with the assertions of McElroy et al. (1976) who extrapolated the Pacific N_2O measurements of Craig and Gordon (1963) to world oceans to conclude that oceans are probably net sinks of N_2O.

The high N_2O synthesis in equatorial waters is not surprising because microbial activity is known to be most pronounced in the warm equatorial regions. What is surprising, however, is the amount of N_2O synthesis in the region of the Pacific Ocean where oxygen content is typically 4 to 4 to 5 ml/l, or an order of magnitude higher than required for efficient denitrification (Hahn and Junge, 1977). This high O_2 content could, however, lead to efficient nitrification processes. It would thus appear that either nitrification processes play a more important role in N_2O synthesis in the ocean than hitherto believed, or denitrification processes are poorly understood and can proceed under conditions that are significantly different from anoxic.

SECTION 7

FLUOROCARBONS-12 AND -11 IN THE GLOBAL ATMOSPHERE

A. Global Emissions

Fluorocarbons-12 and -11 are the two most dominant fluorocarbons in use and have received the most attention. Table 14 shows the global emissions of these chemicals since 1931, when they first came into commercial use. The emissions data are considered accurate to ±5 percent (E. I. du Pont de Nemours, 1978). From Table 14 it is obvious that by the end of 1977 about 5.13 million tons of F-12 and 3.45 million tons of F-11 had been released into the atmosphere. Because of delays associated between production and release, the cumulative emissions at the end of 1977 were about 86 percent of the production for both F-12 and F-11. We should emphasize that it would only be a matter of time before the remaining 14 percent would be released. The best current estimate also suggests that 96 percent of the total release of fluorocarbons-12 and -11 occurred in the northern hemisphere and the remaining 4 percent in the southern hemisphere (Baur, 1978).

B. Global Burden and Distribution

Figure 18 shows the global distribution of F-12 and F-11 for late 1977 and a third order polynomial fit to the data. The equations describing the polynomial fit are given in Table 15. The average concentrations within each hemisphere are also shown in Figure 18. The northern hemisphere average concentration of 230 ppt for F-12 is about 9.5 percent higher than the southern hemisphere average value of 210 ppt. Interestingly enough, the northern hemisphere average concentration of 133 ppt for F-11 is also 10 percent higher than the average northern hemisphere concentration of 119 ppt. The global average burden of F-12 and F-11 by the end of 1977 was represented by tropospheric concentrations of 220 ppt and 126 ppt, respectively. These should be compared with the global average concentration of 245 ppt for F-12 and 145 ppt

Table 14

ANNUAL GLOBAL PRODUCTION AND RELEASE OF FLUOROCARBONS-12 AND -11 (In Units of 10^6kg)

Year	F-12*		F-11*	
	Production	Released	Production	Released
1931	0.5	0.0	0.0	0.0
1932	0.1	0.0	0.0	0.0
1933	0.3	0.1	0.0	0.0
1934	0.7	0.2	0.0	0.0
1935	1.0	0.2	0.0	0.0
1936	1.7	0.4	0.1	0.0
1937	3.1	0.6	0.1	0.0
1938	2.8	0.9	0.1	0.0
1939	3.9	1.3	0.1	0.1
1940	4.5	1.7	0.2	0.1
1941	6.3	2.3	0.3	0.1
1942	5.9	2.9	0.3	0.1
1943	8.2	3.5	0.4	0.2
1944	16.7	4.7	0.4	0.2
1945	20.1	6.1	0.4	0.3
1946	16.6	11.9	0.7	0.6
1947	20.1	19.0	1.3	1.2
1948	24.8	22.2	3.0	2.3
1949	26.1	24.2	4.5	3.7
1950	34.6	27.1	6.6	5.4
1951	36.2	30.2	9.1	7.5
1952	37.2	31.5	13.6	10.8
1953	46.5	35.5	17.3	14.7
1954	49.1	40.3	20.9	18.3
1955	57.6	45.2	26.3	22.6
1956	68.7	52.6	32.5	28.2
1957	74.2	59.8	33.9	31.6
1958	73.4	62.6	29.5	29.7
1959	87.6	69.6	35.6	30.3
1960	99.4	83.2	49.7	39.7
1961	108.5	93.2	60.5	51.2
1962	128.1	107.1	78.1	64.1
1963	146.4	125.8	93.3	78.5
1964	170.1	146.6	111.1	93.2
1965	190.1	165.6	122.8	106.3
1966	216.2	184.3	141.0	119.0
1967	242.8	208.3	159.8	135.1
1968	278.8	238.0	184.8	154.6
1969	311.4	270.0	219.8	180.2
1970	336.9	296.2	241.1	205.1
1971	360.5	319.1	266.6	225.4
1972	401.7	348.3	310.5	253.8
1973	447.5	386.2	354.3	290.6
1974	473.6	420.3	377.6	320.9
1975	419.7	412.6	322.5	312.4
1976	449.8	396.3	349.9	303.6
1977	424.4	376.5	330.7	305.6
Total	5934.7	5134.5	4011.2	3447.5

*An estimated 96 percent was released in the northern hemisphere and 4 percent in the southern hemisphere.

Source: E.I. du Pont de Nemours (1978)

Table 15

LEAST-SQUARES ERROR COEFFICIENTS OF A THIRD-ORDER POLYNOMIAL USED TO DEFINE THE GLOBAL DISTRIBUTION OF TRACE CONSTITUENTS

Compound	Coefficients of Polynomial[*]			
	a	b	c	d
N_2O	3.112 (2)[†]	-1.451 (-2)	-3.325 (-4)	-8.675 (-8)
CCl_2F_2 (F12)	2.206 (2)	0.363	1.096 (-3)	-1.574 (-5)
CCl_3F (F11)	1.290 (2)	0.498	-3.178 (-3)	-8.510 (-5)
CCl_2FCClF_2 (F113)	1.787 (1)	5.249 (-2)	2.346 (-4)	-6.662 (-6)
$CClF_2CClF_2$ (F114)	1.153 (1)	5.591 (-2)	-4.059 (-4)	-7.693 (-6)
$CHCl_2F$ (F21)	4.212	2.952 (-2)	5.583 (-5)	-3.038 (-6)
SF_6	0.292	9.221 (-4)	-5.817 (-6)	1.370 (-7)
CCl_4	1.198 (2)	4.412 (-2)	6.337 (-4)	4.967 (-6)
CH_3CCl_3	8.971 (1)	0.818	7.584 (-4)	-7.894 (-5)
CH_3Cl	6.190 (2)	0.697	-3.128 (-3)	-1.204 (-4)
CH_3I	1.711	-9.422 (-3)	6.931 (-4)	-5.878 (-6)
CH_4	1.409 (3)	0.828	4.435 (-5)	-8.113 (-5)
C_2H_6	0.769	9.926 (-3)	6.526 (-5)	5.561 (-8)

[*] The polynomial is $Y = a+bL+CL^2+dL^3$, where Y is the concentration in ppt for all species except N_2O, CH_4, and C_2H_6, for which it is ppb. The independent variable L is the latitude in degrees and varies from -90° to +64° (N.H. = 0 to +90°, S.H. = 0 to -90°).

[†] $3.112\ (2) = 3.112 \times 10^2$.

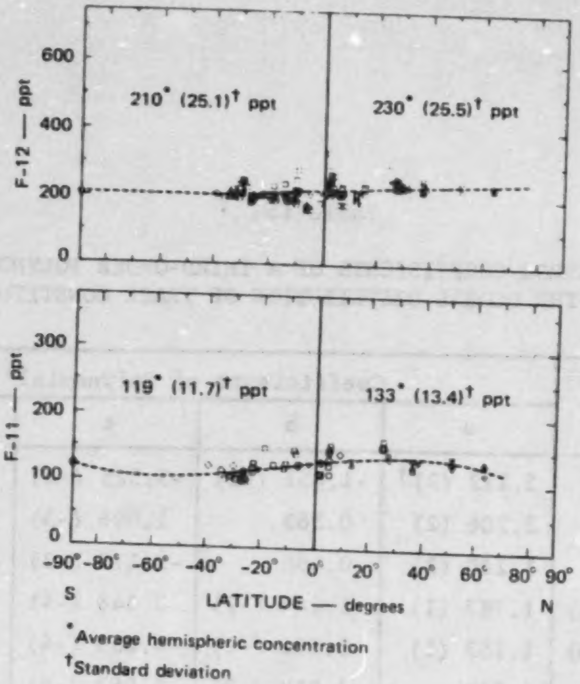


FIGURE 18 GLOBAL DISTRIBUTION OF FLUOROCARBONS-12 AND-11

for F-11 that would result if the cumulative emissions were to be uniformly mixed in the global atmosphere. Clearly, our data would suggest that some loss has indeed taken place.

C. Atmospheric Growth

It is also clear from Figure 18 that within each hemisphere the concentration of F-12 and F-11 is essentially uniform. Thus, any latitude, especially the temperate latitudes from 30-60°, can be adequately used to characterize the hemisphere. Figure 19 shows the average growth rate of F-12 and F-11 based on several field studies conducted between 35 and 45°N latitude. The dotted lines in Figure 19 represent the burden and growth in the northern hemisphere that would result from man-made sources in the absence of any removal mechanisms. It is clear from Figure 19 that the atmospheric burden of F-12 and F-11 between 1975 and 1978 increased at an average rate of 22 ppt/year and 14 ppt/year, respectively. Using late 1975 as the base, this represents an average linear growth rate of 11 percent/yr and 13 percent/yr

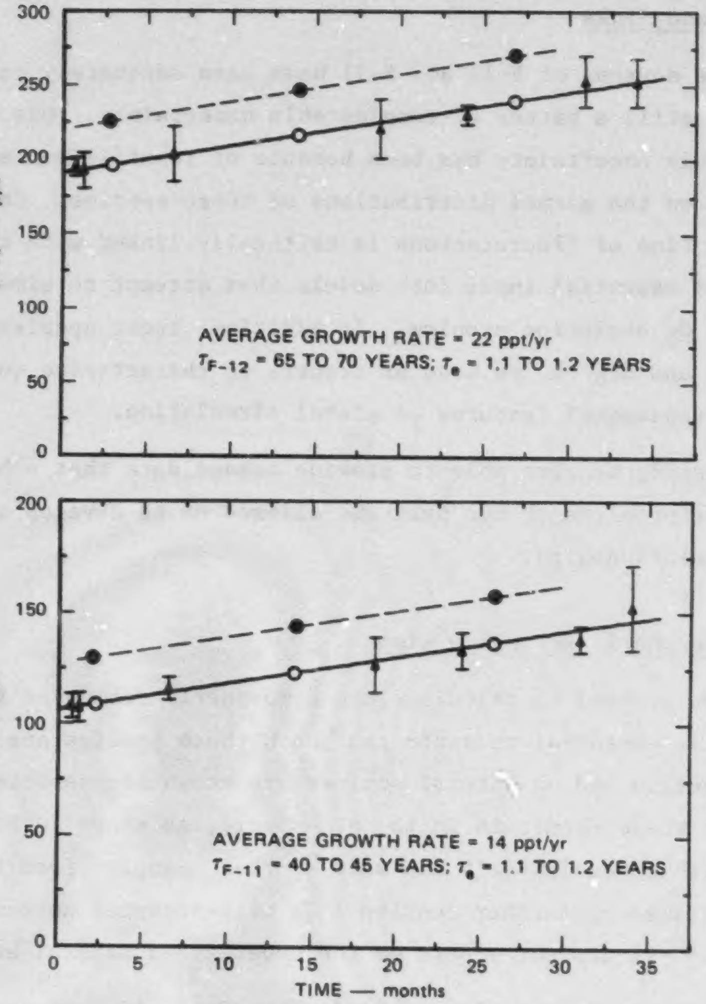


FIGURE 19 ATMOSPHERIC GROWTH AND RESIDENCE TIMES OF FLUOROCARBONS 12 AND 11

Time period beginning 1 November 1975

for F-12 and F-11, respectively. The corresponding emissions burdens increased similarly. The difference between the dashed and the solid lines in Figure 19 is indicative of the amount lost to atmospheric sinks.

D. Sources and Sinks

While the sources of F-12 and F-11 have been adequately characterized, the sinks are still a matter of considerable uncertainty. One of the major reasons for this uncertainty has been because of insufficient and often conflicting data on the global distributions of these species. Calculation of the residence time of fluorocarbons is critically linked with this distribution and is an essential input into models that attempt to simulate the stratospheric O_3 depletion problem. In addition, inert species such as fluorocarbons and SF_6 can be used as tracers to characterize quantitatively some of the fundamental features of global circulation.

In this study we were able to provide needed data that substantially alleviated the problems of the past and allowed us to develop quantitative source-sink relationships.

1. Atmospheric Residence Times

Before we proceed to calculate the atmospheric residence times of F-12 and F-11, it is essential to state that both these species are completely man-made in origin and no natural sources are known or suspected to exist. The growth of these chemicals in the atmosphere, as shown in Figure 19, is also consistent with an exclusively man-made source. Samples from the past decades, although very scarce, further confirm this well-accepted notion that fluorocarbons-12 and -11 are not a part of the unperturbed natural atmosphere.

The only known destruction mechanism for F-12 and F-11 is photolysis in the stratosphere. F-12 and F-11 are not photolyzed in the troposphere and do not react with free radicals. No tropospheric sinks of any significance are either known or postulated. However, it has always been speculated that as yet unknown removal mechanisms for F-12 and F-11 may exist and prevent these chemicals from entering the stratosphere in significant quantities. Data collected in this study provided the best means to assess the question of unknown sinks by the determination of residence times from budget and growth considerations.

It is clear from Figure 18 that both F-12 and F-11 are relatively uniformly distributed in the northern and southern hemispheres. This allows the use of a simplified two-box model to describe the burden of F-12 and F-11 in the northern hemisphere and the southern hemisphere. The two-box model can be mathematically described as follows:

If N and S are the cumulative masses and τ_{in} and τ_{is} are the residence times (years) of any given species i at time τ in the northern and southern hemispheres, respectively, then

$$\frac{dN_i}{dt} = F_{in} - \frac{N_i}{\tau_{in}} - \frac{(N_i - S_i)}{\tau_e} \quad , \tag{2}$$

$$\frac{dS_i}{dt} = F_{is} - \frac{S_i}{\tau_{is}} + \frac{(N_i - S_i)}{\tau_e} \quad , \tag{3}$$

where τ_e is the interhemispheric exchange rate and F_{in} and F_{is} describe the emissions of species i in the northern and the southern hemispheres, respectively.

In the case of fluorocarbons-12 and -11, it is reasonable to assume that $\tau_{in} = \tau_{is}$. Adding equations (2) and (3) we get

$$\frac{dM_i}{dt} = F_i - \frac{M_i}{\tau_i} \tag{4}$$

where $M_i = N_i + S_i$; $F_i = F_{in} + F_{is}$, and $\tau_i = \tau_{in} = \tau_{is}$. In the case of F-12 and F-11, the initial condition is $M_i = 0$ at $t = 0$ (year 1930).

The global emissions data for F-12 and F-11 (F_i) is accurately known (±5 percent) and is reported in Table 14. Equation (4) can be easily solved with the help of a computer program for known values of τ_i. The selected τ_i is the value when modeled and measured estimates of the F-12 and F-11 atmospheric burden agree.

Since most of the measurements we made were conducted in the northern hemisphere, we show these results for the northern hemisphere in Figure 19.

The quantity N_i is estimated by using Equation 4 and the measured distribution of F-12 and F-11 in the northern and southern hemispheres ($N_{F-12} = 1.095\ S_{F-12}$; $N_{F-11} = 1.118\ S_{F-11}$).

The solid line in Figure 19 shows the average growth based on data measured in the northern hemisphere, a region of essentially uniform concentration. The dashed line indicates the concentration in the northern hemisphere that would result if the cumulative emissions were distributed globally according to the distribution shown in Figure 18. The difference between the dashed and the solid lines is indicative of the amount lost to atmospheric sinks. The circles indicate the predicted concentration in the northern hemisphere from emissions data and the range of indicated residence times. It is clear from Figure 19 that residence times of 65 to 70 years for F-12 and 40 to 45 years for F-11 best fit the observational data.

2. Calculation of a Mean Interhemispheric Exchange Rate

Once the residence times for F-12 and F-11 are calculated, it is easy to solve Equations (2) and (3) simultaneously to determine an average value for the interhemispheric exchange rate (τ_e). Here we compared the measured distribution of F-12 and F-11 in the two hemispheres with that predicted by Equations (2) and (3). Since our interhemispheric data was obtained in late 1977, convergence was sought only for that time. As should be expected, the model did reflect some changes in the north-south distribution of F-12 and F-11 with time. This was mainly because of the changing emission patterns of F-12 and F-11.

The north-south distribution of F-12 and F-11 shown in Figure 18 ($N_{F-12}/S_{F-12} = 1.095$; $N_{F-11}/S_{F-11} = 1.118$) were best described by a τ_e of 1.1 to 1.2 years, as shown in Figure 19. This estimate of τ_e is in good agreement with recommended estimates of Czeplak and Junge (1974) but in disagreement with other studies that calculate a τ_e of 2 to 4 years (Czeplak and Junge, 1974). Thus, the fluorocarbon data suggest that the northern hemisphere and southern hemisphere air masses are exchanged in a relatively fast time of 1.2 years.

3. Oceanic Sink

It has also been postulated that fluorocarbons-12 and -11 may find a potential sink in the oceans. During our Pacific trip we analyzed a limited number of surface-water samples to assess the role of oceans, in a preliminary fashion, as a source or a sink for halocarbons.

Table 16 shows data for the concentration of F-12 between 0- and 300-m depths at intervals of 50 m. The average surface-water halocarbon concentrations as they vary with latitude (0- to 2-m depth) and the 300-m concentration data are summarized in Table 17. The average measured surface-water concentrations of F-12 and F-11 were 0.28 and 0.13 ng/liter, respectively. With the surface-water concentrations of halocarbons known, a simple film-diffusion model described in Equation 1 can be applied to estimate the flux of halocarbons into or out of the ocean. Solubility data for F-12 and F-11 from Junge (1976) suggest that if the surface water is in equilibrium with the atmospheric burden, the concentrations of F-12 and F-11 in water should be about 0.05 and 0.06 ng/liter, respectively. These concentrations are lower than the measured average concentrations of 0.28 and 0.13 ng/liter, so it appears that ocean water is supersaturated with F-12 and F-11. This means that either the solubility data are inaccurate or the water samples were inadvertently contaminated. It is also possible that the ocean surface waters have been contaminated by man-made activities on a global scale. The lowest concentration of F-12 and F-11 measured (Table 17), 0.07 ng/liter, is about what one would expect if the surface water were saturated with F-12 and F-11. If the surface water were saturated, the ocean would be a relatively ineffective sink for F-12 and F-11 but could act as a reservoir containing less than 0.5 percent of the atmospheric burden of F-12 and F-11 in a steady-state situation.

E. Discussion of Results

Atmospheric residence times of 65 to 70 years for F-12 and 40 to 45 years for F-11 best fit the observational data. These long residence times can be accounted for from the stratospheric photolytic loss alone, and rule out the possibility of any significant missing sinks that may prevent these fluorocarbons from entering the stratosphere almost in their entirety.

Table 16

F-12 CONCENTRATIONS IN THE PACIFIC OCEAN

Depth (m)	Date 11-25-77 Lat 19°02'N Long 137°46'W		Date 11-27-77 Lat 11°52'N Long 142°25'W		Date 11-30-77 Lat 01°26'S Long 150°10'W		Date 12-6-77 Lat 25°40'S Long 167°33'W		Date 12-8-77 Lat 33°40'S Long 173°50'W		Date 12-11-77 Lat 39°05'S Long 179°13'W	
	ng/1	Temp (°C)	ng/1	Temp (°C)	ng/1	Temp (°C)	ng/1	Temp (°C)	ng/1	Temp (°C)	ng/1	Temp (°C)
0	0.40	24.3	0.32	25.4	0.35	27.6	0.25	23.2	0.19	18.5	0.53	16.9
50	0.20	24.0	0.23	17.4	0.25	27.5	0.20	21.8	0.20	14.6	0.18	16.8
100	0.32	24.0	0.23	12.2	0.28	27.5	0.20	19.4	0.22	13.5	0.10	14.7
150	0.15	20.6	0.56	11.8	0.33	25.8	0.25	18.5	0.25	12.7	0.09	13.7
200	0.15	19.2	0.42	11.1	0.31	19.0	0.25	17.7	0.24	12.2	0.09	13.4
250	0.22	17.3	0.24	10.6	0.24	13.6	0.45	16.3	0.27	11.7	0.09	13.1
300	0.20	12.4	0.07	10.2	0.24	13.4	0.45	15.2	--	10.7	0.09	13.0

Table 17

CONCENTRATIONS OF HALOCARBONS IN PACIFIC SEAWATER

Date	Lat	Long	Water Temp (°C)	Concentration (ηg/1)				
				F12	F11	CCl_4	CH_3Cl	$CHCl_3$
11-25-77	19°02'N	137°48'W	24.3	0.40	--	--	--	--
11-26-77	15°43'N	140°05'W	25.5	0.32	--	--	--	--
11-27-77	11°52'N	142°25'W	25.4	0.32	--	--	--	--
11-28-77	06°35'N	145°14'W	28.4	0.47	--	--	--	--
11-29-77	02°35'N	145°14'W	26.5	0.07	--	--	--	--
11-30-77	01°26'S	150°10'W	27.6	0.35	--	--	--	--
12-01-77	06°07'S	153°13'W	28.1	0.14	--	--	--	--
12-02-77	09°07'S	155°75'W	28.8	0.07	0.15	0.41	34.5	<0.05
12-04-77	18°24'S	161°42'W	26.7	0.14	0.24	0.45	85.8	<0.05
12-06-77	25°40'S	167°33'W	23.2	0.25	0.07	0.35	21.2	<0.05
12-07-77	30°14'S	171°18'W	21.5	0.40	0.10	0.38	1.4	<0.05
12-08-77	33°40'S	173°50'W	18.5	0.19	0.10	0.40	12.5	<0.05
12-11-77	39°05'S	179°13'W	16.9	0.53	0.12	0.40	5.3	<0.05
Average Surface (0-2 m) concentration				0.28 ± 0.15	0.13 ± 0.06	0.40 ± 0.03	26.8 ± 31.2	<0.05
Average 300-m Concentration				0.21	0.06	0.15	3.3	<0.05

Jesson et al. (1977) have calculated a F-11 residence time of 10 to 20 years and implied missing sinks for F-11. We attribute this difference to the use of southern hemisphere data as measured by Lovelock et al. (1973) in 1972, in which the southern hemisphere concentrations of F-11 were only half the northern hemisphere values. Our measurements of the global distribution of five fluorinated species confirm that the southern hemisphere concentrations of all inert species, including F-12 and F-11, are only about 10 percent lower than the northern hemisphere values and, contrary to the findings of Lovelock et al. (1973), no gradients within each hemisphere exist. In addition, analysis of Lovelock's F-11 data would suggest a τ_e of more than 2 years. This is not supported by available information (Czeplak and Junge, 1974). Thus, overall budget considerations do not allow for the postulation of major sinks for F-12 and F-11, and the oceans certainly do not appear to be such a sink. The reasons for the supersaturation of oceanic waters with F-12 and F-11 currently cannot be understood.

SECTION 8

FLUOROCARBONS-22, -113, -114, -21 AND SF_6 IN THE GLOBAL ATMOSPHERE

A. Global Emissions

The emissions data for F-22, the third most commonly used fluorocarbon, is given in Table 18. By the end of 1977, 0.93 million tons of F-22 had been produced and about 0.43 million tons or 46 percent had been released. Unlike F-12 and F-11, nearly all of F-22 is used as a refrigerant. In such applications, long delay times between production and release can be expected. The remaining 54 percent of F-22 produced would eventually be released to the atmosphere.

Accurate emissions data for F-113, F-114, F-21 and SF_6 are currently not available. Production estimates suggest that cumulative F-113 production by the end of 1977 was about 0.7 million tons, and about 0.6 million tons of F-113 were released. Since almost all of the F-113 is used in solvent applications, there are no long-term delay periods in production and end usage. F-114, on the other hand, finds a major application as a refrigerant. We estimate that by the end of 1977 about 0.3 million tons of F-114 had been produced and about 0.25 million tons had been released. Fluorocarbon-21 is a very minor industrial product. Release estimates through 1977 from known product and by-product sources are probably less than 0.6 million kg, though large unknown sources of F-21 may exist. The total SF_6 released to date can be roughly estimated to be somewhere between 20 and 40 million kg.

B. Global Burden and Distribution

The global distribution of F-22 has not yet been characterized because of measurement difficulties. No atmospheric data on F-22 are available from any source. Our limited attempts involving preconcentration of large amounts of air samples during this study suggested F-22 levels in the neighborhood of 20 to 30 ppt in clean background air. Poor sensitivity of F-22 to electron

Table 18

ANNUAL GLOBAL PRODUCTION AND RELEASE OF FLUOROCARBON-22
(in units of 10^6 kg)

Year	Production	Release
1931	0.0	0.9
1932	0.0	0.0
1933	0.0	0.0
1934	0.0	0.0
1935	0.0	0.0
1936	0.0	0.0
1937	0.0	0.0
1938	0.0	0.0
1939	0.0	0.0
1940	0.0	0.0
1941	0.0	0.0
1942	0.0	0.0
1943	0.0	0.0
1944	0.0	0.0
1945	0.1	0.0
1946	0.0	0.0
1947	0.1	0.0
1948	0.2	0.0
1949	0.3	0.1
1950	0.8	0.1
1951	1.0	0.2
1952	1.6	0.3
1953	2.2	0.4
1954	2.9	0.6
1955	3.7	0.8
1956	6.1	1.2
1957	6.3	1.1
1958	7.6	1.4
1959	11.2	2.7
1960	12.2	3.3
1961	12.2	3.6
1962	15.4	4.6
1963	17.6	5.6
1964	22.4	6.8
1965	25.1	8.1
1966	31.5	9.8
1967	37.3	12.3
1968	45.6	16.3
1969	55.9	20.3
1970	58.6	23.2
1971	64.5	26.2
1972	70.0	30.9
1973	76.5	35.7
1974	87.7	41.8
1975	73.6	47.1
1976	94.1	60.2
1977	101.9	65.2
Total	946.2	429.9

Source: Bauer (1978)

capture has made its measurement difficult. It also appeared that F-22 was significantly destroyed on Ascarite traps. At this time no reliable atmospheric data base for F-22 exists.

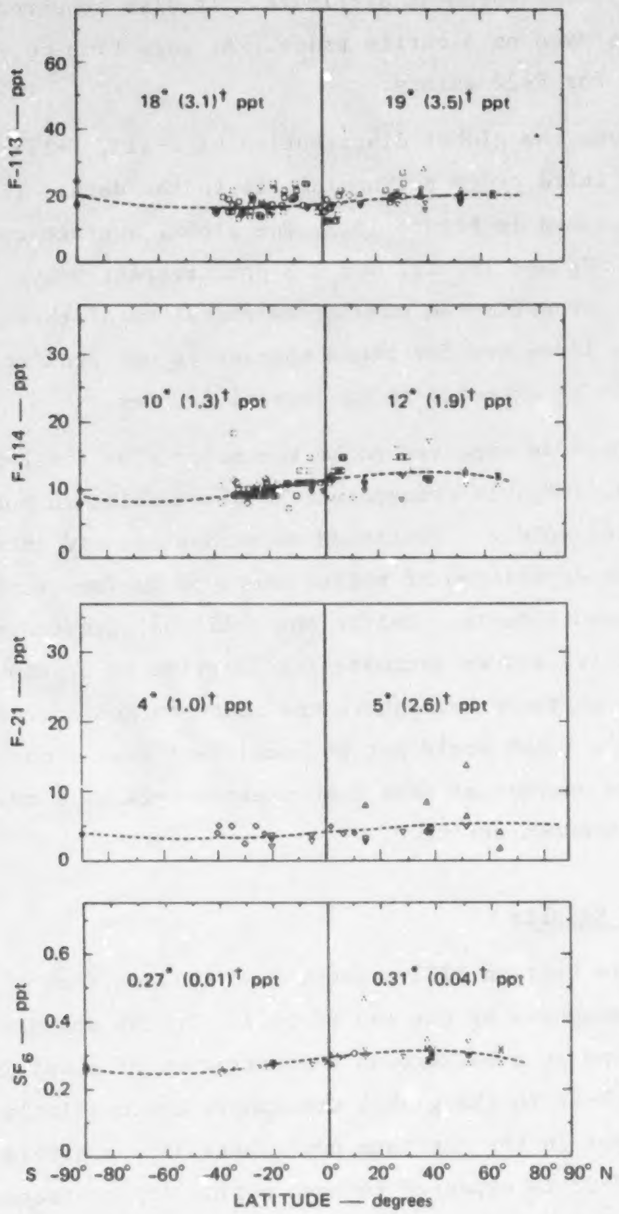
Figure 20 shows the global distribution of F-113, F-114, F-21, and SF_6, and illustrates a third order polynomial fit to the data. (The nature of the polynomial is described in Figure 15.) The global average concentrations of F-113, F-114, and SF_6 are 18, 11, and 0.3 ppt, respectively. These values are comparable to the estimated cumulative emissions of these species. An accurate emissions inventory for these species is not available, but their residence times can be expected to be several decades.

The stratosphere is expected to be the major sink for F-113 and F-114. Sulfur hexafluoride (SF_6) is transparent to ultraviolet in both the troposphere and the stratosphere. Continued emissions of, and increases in, SF_6 could result in the deposition of sulfur above 50 km (destruction via electron capture) with unknown effects. Unlike the fully halogenated fluorocarbons, F-21 is quite reactive and we estimate its lifetime to be about 4 years (see Section XVI). The northern hemisphere and southern hemisphere concentrations of 5 ± 3 ppt and 4 ± 1 ppt would not be consistent with a northern hemisphere source. It remains unclear at this time whether F-21 is a true atmospheric constituent or an unknown artifact.

C. Discussion of Results

As estimated in Section VIII-A about 0.43 million tons of F-22 had been released to the atmosphere by the end of 1977. In the absence of any sinks this would correspond to a background concentration of about 29 ppt. However, no measurements of F-22 in the global atmosphere are available. Our measured value of 20 to 30 ppt in the northern hemisphere is comparable to the estimated emissions. F-22 is expected to have a sink in the troposphere via reaction with HO. However this removal process is extremely slow and can provide a residence time of about 35 years in the troposphere (see Section XVI).

No tropospheric sinks for F-113 and F-114 of any significance are known. Their structural similarity to F-11 and F-12 would also preclude the existence of dominant sinks. Photochemical destruction in the stratosphere is the only known removal mechanism. The atmospheric residence times of F-113 and F-114



*Average hemispheric concentrations

†Standard deviation

FIGURE 20 GLOBAL DISTRIBUTIONS OF F-113, F-114, F-21, AND SF$_6$

can be expected to be greater than 40 years. The cumulative emissions of F-113 and F-114 are estimated to be 0.6 million tons and 0.3 million tons, respectively. If these were to be globally distributed instantly, an average background concentration of 19 ppt for F-113 and 9 ppt for F-114 would result. This is in excellent agreement with the measured global average concentration of 18 ppb and 11 ppt, respectively, for F-113 and F-114. The agreement is somewhat fortuitous since the emissions data for F-113 and F-114 are rather approximate.

SF_6 is present in extremely small quantities and is an excellent tracer of atmospheric motions. We do not expect SF_6 to have any significant sinks in the troposphere or the stratosphere. Unlike chlorinated species, fully fluorinated species (e.g., SF_6, CF_4) appear to be transparent to UV even in the stratosphere. The major sink for SF_6 is likely to be because of destruction by electron absorption in the ionosphere. Injections of sulfur and/or fluorine in the ionosphere may have an unknown environmental impact. In the meantime, the atmospheric burden of SF_6 continues to increase at a rate of 5 to 10 percent/year.

Since the first reported measurement of F-21 (Singh et al., 1977c), some researchers have speculated whether or not F-21 is a product of F-11 decomposition in the troposphere. This possibility has been advanced because of two major considerations:

- The direct emissions of F-21 appear to be so low that they could not account for more than 0.1 ppt of atmospheric F-21.
- Laboratory experiments do show some thermal and photochemical decomposition of F-11 on sand with F-21 as one of the products of decomposition.

Both of these observations are based on qualitative evidence that is not easy to extend to the atmosphere. Indeed, secondary sources of F-21 may exist but have not yet been adequately characterized. Recent experiments conducted in Italy have used mass fragementometry to confirm the identity of F-21.

It is therefore acknowledged that more information on F-21 is needed to characterize adequately its role in the atmosphere. In the meantime, it is possible to estimate the significance of F-21 as a sink for F-11 by using a simplified model.

$$\text{F-11} \xrightarrow{k_1} \text{F-21} \xrightarrow{k_2} \begin{array}{l}\text{unknown}\\ \text{products}\end{array} \quad .$$

Assuming F-21 to be in a steady state one can calculate that

$$\frac{\tau^t_{F-11}}{\tau_{F-21}} = \frac{k_2}{k_1} = \frac{[\text{F-11}]}{[\text{F-21}]} \quad . \tag{5}$$

In 1977 the average background concentration of F-11 was 126 ppt and that of F-21 was 4.5 ppt. τ_{F-21} has been estimated to be 4.3 years (see Section XVI). Inserting these in Equation (5) we can calculate a tropospheric F-11 residence time (τ^t_{F-11}) of 125 years. Thus, even if the postulate that F-21 is a product of F-11 decomposition is correct, this tropospheric sink would be relatively small. The possibility that F-21 is truly an atmospheric constituent that is represented by our measurements is yet to be convincingly demonstrated.

SECTION 9

ATMOSPHERIC CARBON TETRACHLORIDE

A. Global Emissions

Unlike the fluorocarbons, the sources of atmospheric CCl_4 have been a matter of considerable uncertainty. Lovelock and coworkers (1973) were the first to suggest that CCl_4 must be of natural origin. These conclusions were based on two observations:

- Their inability to uncover significant man-made emissions.
- The global distribution of CCl_4 was much more uniform that F-11

Thus, up until late 1975 the emissions of CCl_4 were believed to be negligibly small and it was considered to be a species of natural origin. When attempts were made to develop an emissions data base it became clear that large amounts of CCl_4 had been released to the atmosphere between 1930 and 1960. Indeed, it appeared that CCl_4 was predominantly of man-made origin. Three almost simultaneous and independent attempts at quantifying the sources of CCl_4 (Altshuller, 1976; Singh et al., 1976a; Galbally, 1976) arrived at nearly identical conclusions. Here we shall describe our results (Singh et al., 1976a) with the proviso that these are not significantly different from the results of the other two investigators.

Figure 21 shows the yearly production and release data for CCl_4 for the United States, Western Europe, and Japan. The global emissions were estimated to be 1.1 times the emissions from these three regions. Details of these estimates and the sources of information have already been published (Singh et al., 1976a). Table 19 has been constructed from the same data used to plot Figure 21. When year to year details were not available, data between years was interpolated. It is clear from Figure 21 and Table 19 that an estimated 3.04 million tons of CCl_4 has been released to date and over 75 percent of these emissions have originated in the United States. It should also be added that secondary sources of CCl_4 are known to exist but are much harder to

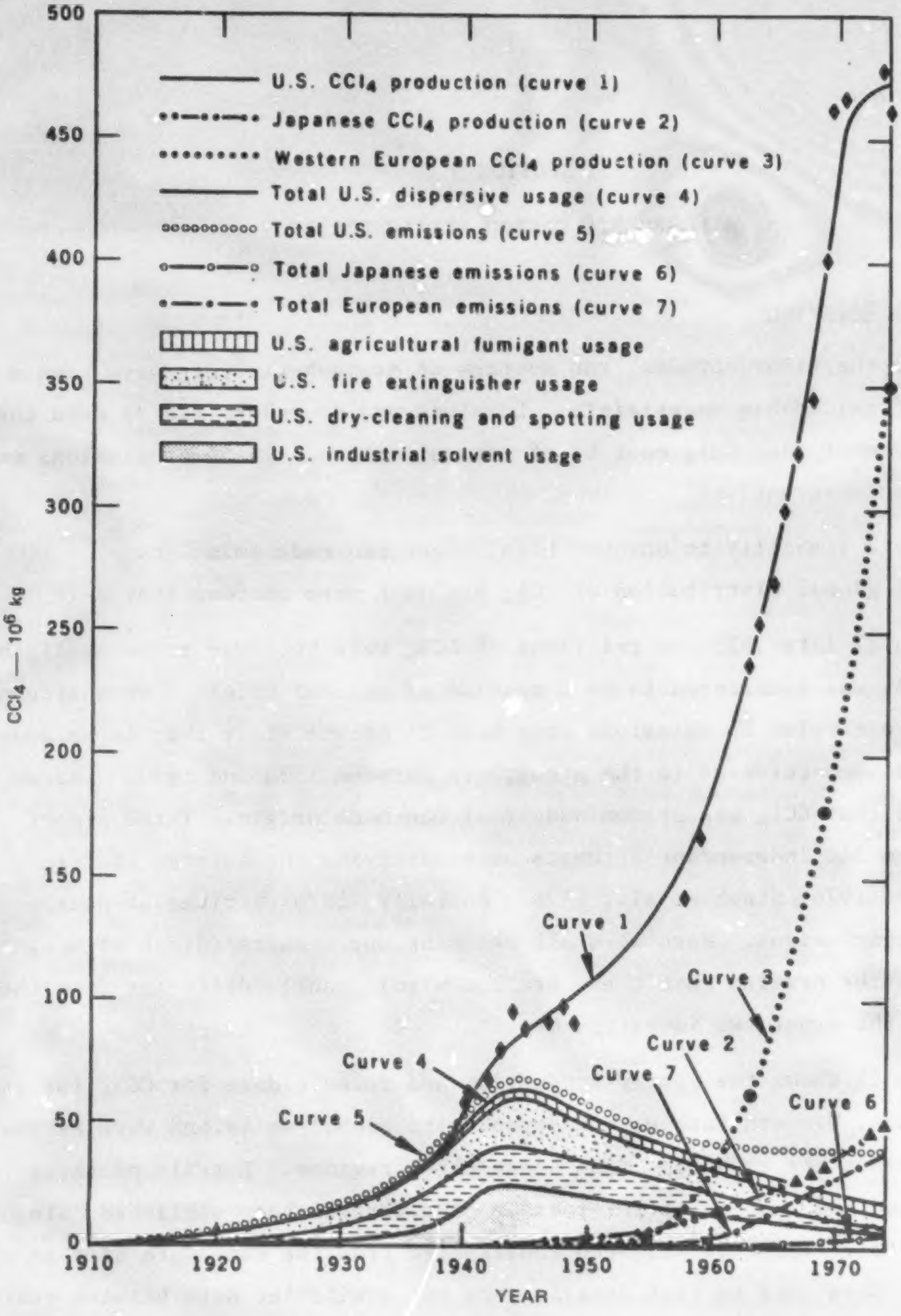


FIGURE 21 PRODUCTION AND EMISSION TRENDS FOR CCl_4

Table 19

ANNUAL GLOBAL CCL$_4$ RELEASE SINCE 1910
(in 10^6 kg/year)

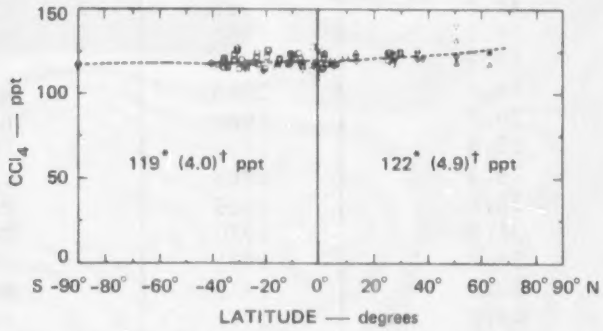
Year	CCl$_4$ Release	Year	CCl$_4$ Release
1910	0.0	1945	75.0
1911	0.5	1946	74.5
1912	1.1	1947	72.6
1913	1.6	1948	70.6
1914	2.2	1949	67.9
1915	3.3	1950	65.2
1916	4.4	1951	63.0
1917	5.0	1952	60.8
1918	5.5	1953	58.6
1919	6.6	1954	56.5
1920	7.7	1955	54.8
1921	8.8	1956	53.2
1922	9.9	1957	52.7
1923	10.0	1958	52.2
1924	10.1	1959	53.0
1925	11.6	1960	53.9
1926	13.2	1961	54.4
1927	14.8	1962	55.0
1928	16.5	1963	56.6
1929	18.2	1964	58.3
1930	19.8	1965	62.2
1931	20.9	1966	66.0
1932	22.0	1967	68.8
1933	25.3	1968	71.5
1934	28.6	1969	75.4
1935	31.9	1970	79.2
1936	35.2	1971	82.0
1937	40.7	1972	84.7
1938	46.2	1973	89.1
1939	52.2	1974	94.0
1940	58.3	1975	85.0
1941	63.8	1976	81.0
1942	69.3	1977	82.0
1943	72.4	Total	3037.3
1944	75.5		

Source: Singh et al. (1976)

quantify. Chlorination of water and accidental spillage of large amounts of CCl_4, which are often not reported, are only two sources that are not included in Table 19. The possibility that some 8 percent of the C_2Cl_4 released to the atmosphere may be converted to CCl_4 has also been proposed (Singh et al., 1975) based on laboratory smog-chamber data. This source alone could account for up to 0.7 million tons of CCl_4. However, the applicability of these laboratory results to the real atmosphere are still in question and therefore not included in Table 19. We suspect that the CCl_4 emissions inventory could be an underestimate by as much as 30 percent. No natural sources of CCl_4 are known to exist.

B. Global Burden and Distribution

Figure 22 clearly shows that unlike fluorocarbons, CCl_4 is rather uniformly distributed with a northern hemisphere and southern hemisphere concentration difference of 2.5 percent. The global average concentration of 120 ppt is indicated from Figure 22. This corresponds to an atmospheric burden of 3.2 million tons. (A third order polynomial used to fit the global distribution of CCl_4 is described in Table 15.)



*Average hemispheric concentrations

†Standard deviation

FIGURE 22 GLOBAL DISTRIBUTION OF CARBON TETRACHLORIDE

C. Atmospheric Growth

Figure 23 shows a small average growth rate of about 3 ppt/year during the period 1975 and 1978. It appears from our measurements that the growth rate of CCl_4 is only about a quarter of the fluorocarbon growth rates.

D. Sources and Sinks

1. Atmospheric Residence Time

Since the emissions data for CCl_4 are not highly accurate and all the sources are not characterized, it is not possible to determine the residence time of CCl_4 directly. Therefore, here we shall use direct information on sinks to estimate the residence times of CCl_4.

The global background CCl_4 concentration of 120 ppt that we measured corresponds to an atmospheric burden of 3.2 million tons. The known emissions reported in Table 19 are estimated to be 3.0 million tons. Thus, an inconsistency exists and must be attributed to inaccuracies in the emissions inventory, largely from sources that currently cannot be quantified.

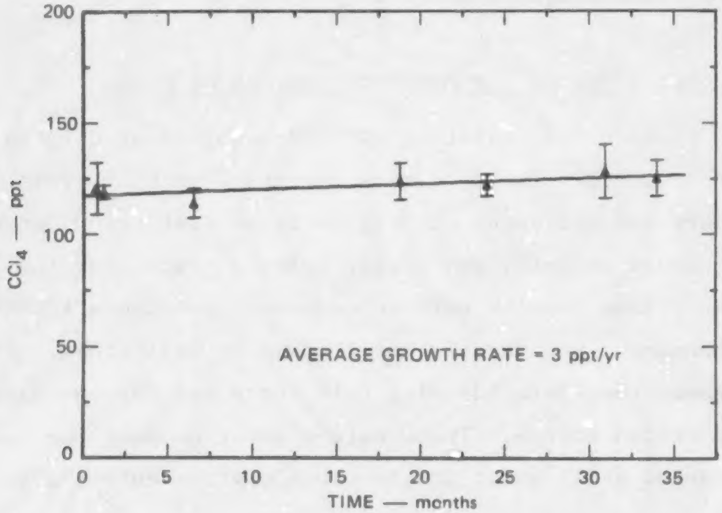


FIGURE 23 ATMOSPHERIC GROWTH OF CCl_4 IN THE NORTHERN HEMISPHERE

Time period beginning 1 November 1975

The stratosphere is by far the most important sink for CCl_4. The inertness of CCl_4 in the troposphere is well known and its lifetime here has been estimated to be in excess of 300 years. The stratospheric sink from photolysis is estimated to be between 50 and 75 years. Figure 24 shows the atmospheric burden of CCl_4 based on a 50-year residence time. Curve 5 shows the net calculated worldwide profile of CCl_4 cumulative atmospheric loading, resulting solely from emissions from anthropogenic sources with concurrent removal by transport to the stratosphere and photolysis.

It is clear from Figure 24 that the cumulative build-up of CCl_4 from known anthropogenic sources up to 1973, was about 1.9 million tons or about 72 ppt. When extrapolated to 1977 this predicted value would be about 2.1 million tons or about 80 ppt. Thus, known emissions data, when coupled with a 50-year atmospheric residence time, can account for 80 ppt of CCl_4. This can be compared with an actual atmospheric abundance of 120 ppt. Therefore, about a third of the atmospheric CCl_4 is currently unaccounted for. Furthermore, examination of the atmospheric accumulation rate of CCl_4 (curve 5) and that of F-11 (curve 6) reveals that 65 percent of the total CCl_4 released to the atmosphere was emitted before 1960, whereas 96 percent of the F-11 was released after 1960. This additional time available to CCl_4 for global dispersion and its slow release to the atmosphere explains the relative global uniformity of CCl_4 as compared with F-11.

a. Other Evidence for Man-Made Sources of CCl_4

Another way to ascertain existing man-made sources of CCl_4 is through actual field measurements. Based on measurements from California (site 2) we clearly demonstrated instances of CCl_4 increase that coincided with a corresponding increase in F-12, the latter being an excellent indicator of urban air masses. These results were subsequently published (Singh et al., 1977a). The phenomenon, however, is not limited to California. Figure 25 shows CCl_4 increases that coincide with F-11 increases for two days of data from the eastern United States. These data clearly support the view that man-made CCl_4 sources still exist in the urban environments within the United States.

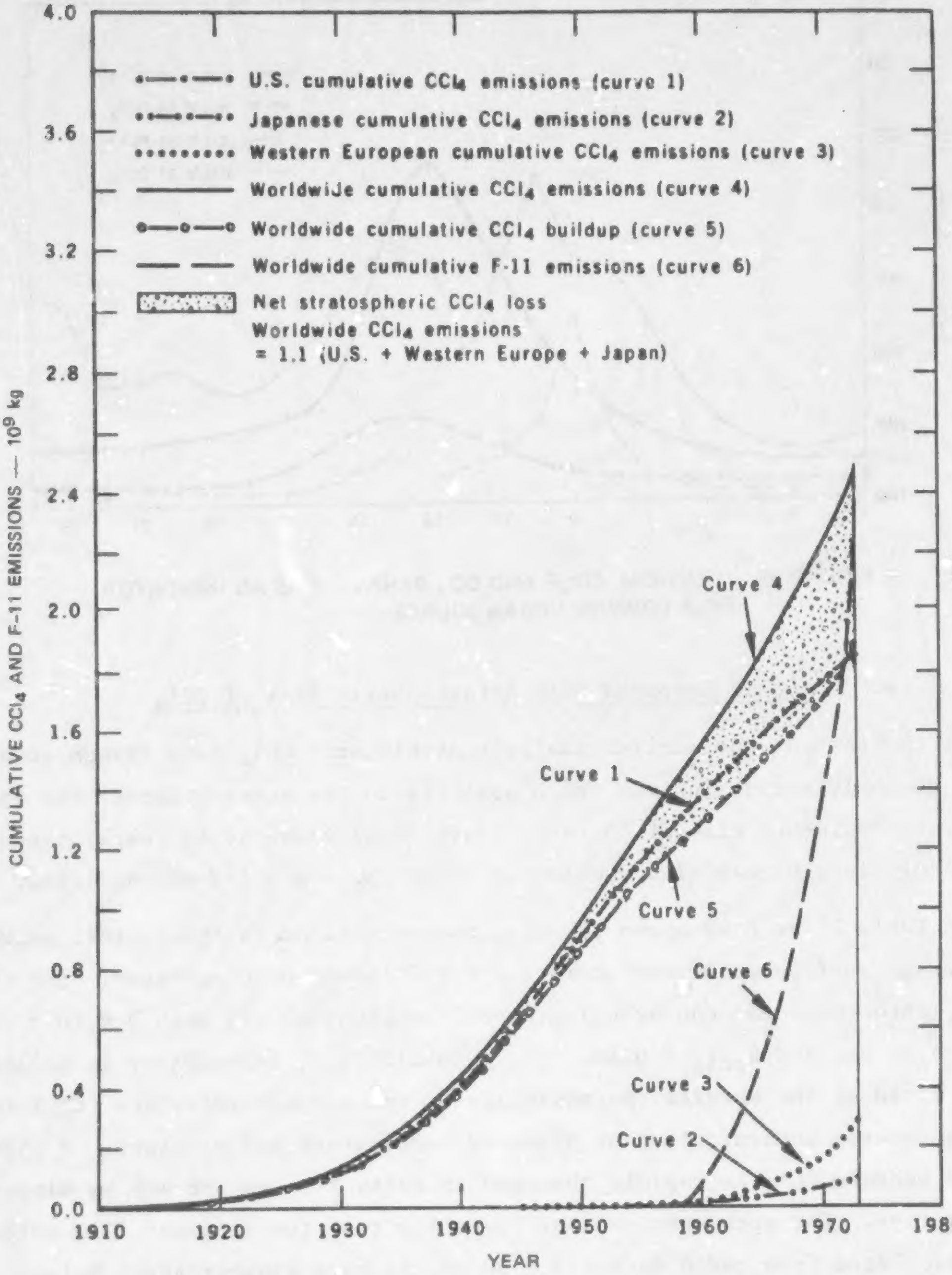


FIGURE 24 CUMULATIVE CCl_4 AND F-11 EMISSIONS

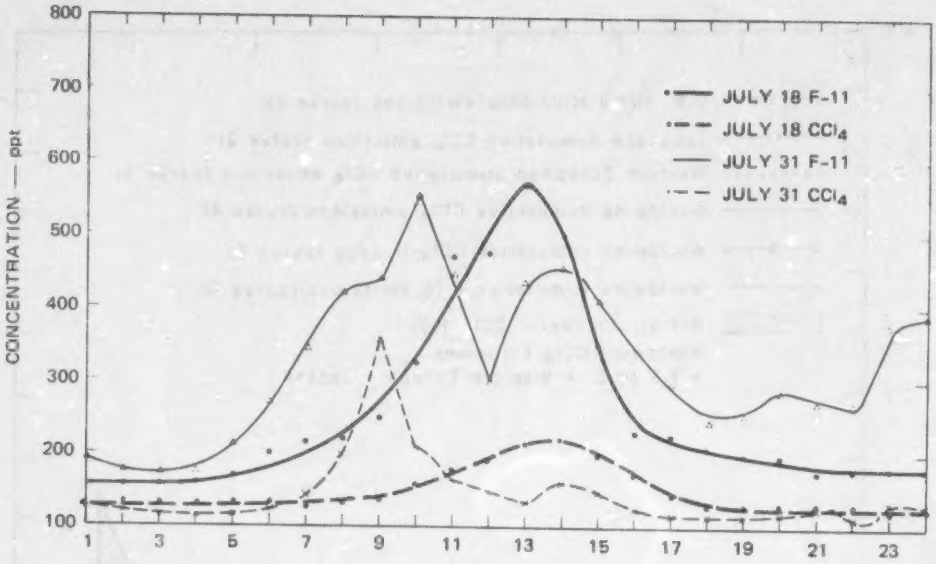


FIGURE 25 IDENTICAL CCl_3F AND CCl_4 BEHAVIOR AS AN INDICATOR OF A COMMON URBAN SOURCE

b. Oceanic Compared With Stratospheric Sink of CCl_4

At the time of our earlier analysis of historic CCl_4 data (Singh et al., 1976a) the only known sink was the photolysis in the stratosphere. The estimated CCl_4 residence time of 50 to 75 years (best value of 60 years) based on the photolytic sink was also considered to be the overall residence time.

In Table 17 we have shown the CCl_4 concentrations in the Pacific seawater. The average surface water concentration for CCl_4 was 0.40 ng/liter. The flux of CCl_4 into the ocean can be calculated from Equation (1) with $D = 10^{-5}$ cm^2/sec, $Z = 90$ μm, and $S_{ccl_4} = 0.85$. The solubility, S, in seawater is defined as the ratio of the species concentration at the air-sea interface (C^w_{eq}) to the atmospheric concentration at standard temperature and pressure. A high Z is used because CCl_4 is rapidly absorbed in fatty tissues and may be biologically active. For such species, the upper limit of the stagnant film thickness calculated from radon data (63 ± 30 μm) is more appropriate. Using Equation (1), we can calculate a CCl_4 flux into the ocean of 2.8×10^{-16}g cm^{-2}/sec. If we assume this flux to be typical of all oceans, we obtain an exchange rate of 3.2×10^{10}g/year. The atmospheric burden of CCl_4 from our measurements is calculated as 3.2×10^{12}g. Thus, the ocean is a sink for CCl_4 that can provide a turnover rate of 100 years, as in

$$\tau_o(CCl_4) = \frac{3.2 \times 10^{12}}{3.2 \times 10^{10}} = 100 \text{ years} \quad .$$

Our measurements, although preliminary because of a limited number of samples, do suggest the possibility of an oceanic sink for CCl_4 that is about half as effective as the stratospheric sink. Consequently, it would appear that an overall CCl_4 atmospheric residence time of 35 to 45 years is the best value. Our use of the 50-year residence time may be a slight overestimate.

E. Discussion of Results

Based on our results, our understanding of the atmospheric fate of CCl_4 has undergone a significant change. Prior to our findings, it was believed that CCl_4 was of natural origin, even though no natural sources were known.

More careful quantitation of CCl_4 emissions has shown the following:

- CCl_4 appears to be essentially of man-made origin, and known emissions data, when coupled with known residence time information, can account for about two-thirds of the atmospheric CCl_4 burden. Large unquantified man-made sources of CCl_4 probably exist.
- The atmospheric release of CCl_4 has been at a much slower rate than that of fluorocarbons over a longer period of time. This has allowed CCl_4 to be relatively uniformly distributed in the global atmosphere. The present atmospheric growth of CCl_4 (2 to 3 percent/year) is almost entirely attributable to man-made emissions.
- It is probable that an oceanic CCl_4 sink exists that is about half as effective as the stratospheric sink.

It is pertinent to add that the emissions data for CCl_4 is not of very high quality and most likely underestimates the emissions by as much as 30 percent. The arguments used to suggest a natural origin of CCl_4 are no longer valid. The bulk of the evidence points to dominant man-made sources.

SECTION 10

ATMOSPHERIC METHYL CHLOROFORM

Methyl chloroform (CH_3CCl_3) is a commonly used solvent and degreasing agent. It has undergone rapid growth in recent years because it was the recommended substitute for trichloroethylene and tetrachloroethylene, whose usage had been significantly curtailed for toxicity reasons and because of their involvement in producing smog.

Until recently, it was commonly believed that the atmospheric lifetime of CH_3CCl_3 was 1 to 2 years (NAS, 1976) and this was too long to cause photochemical pollution but too short to allow significant amounts to enter the stratosphere. Based on the present study, the fate of CH_3CCl_3 has become a matter of considerable debate. We analyzed our measurements in light of available emissions data to demonstrate the role of CH_3CCl_3 as an indicator of hydroxyl radical and to prove that the lifetime of CH_3CCl_3 is sufficiently long to allow large quantities to enter the stratosphere. In this section we discuss the sources and sinks of CH_3CCl_3 and show how this man-made pollutant provides a unique opportunity to study the chemistry of the natural atmosphere.

A. Global Emissions

The global production and release figures for CH_3CCl_3 are shown in Table 20. The data was provided by Dow Chemical Company and is expected to be accurate to within ±5 percent (Neely and Plonka, 1978; Farber, 1979). Table 20, however, does not include production and release figures from the Soviet Union and East European countries. These emissions are estimated to be less than 5 percent of those reported in Table 20. Plonka (Dow Chemical) suggests that the production figures in Table 20 could be used as an upper limit on the total global emissions of CH_3CCl_3. We have used Plonka's suggestion in the calculations that follow in the subsequent sections, since this also leads to a conservative analysis (shortest residence time).

Table 20

ANNUAL GLOBAL PRODUCTION AND RELEASE RATES OF METHYL CHLOROFORM (in 10^6 kg/yr)

Year	Production	Release
1951	0.1	0.1
1952	0.2	0.2
1953	1	1
1954	3	3
1955	8	8
1956	14	12
1957	21	20
1958	22	21
1959	32	30
1960	38	36
1961	40	38
1962	59	56
1963	58	51
1964	64	57
1965	83	73
1966	116	109
1967	146	131
1968	158	145
1969	168	148
1970	181	155
1971	191	167
1972	267	230
1973	350	340
1974	390	363
1975	374	365
1976	438	416
1977	470	446
Total	3692	3421

Sources: Neely and Plonka (1978); Farber (1979)

As is clear from Table 20, the growth of CH_3CCl_3 has been very rapid. Between 1955 and 1977 an average yearly growth rate of about 16 percent can be calculated. In more recent years this growth rate has been closer to 12 percent. By the end of 1977 about 3.4 million tons of CH_3CCl_3, or about 90 percent of production, had been released. The remaining 10 percent would be released with some delay time. Our best estimate also suggests that 96 percent of CH_3CCl_3 release took place in the northern hemisphere while the remaining 4 percent occurred in the southern hemisphere.

B. Global Burden and Distribution

Figure 26 shows the detailed global distribution that was measured during the conduct of this study. Prior to this all measurements were point measurements and most of these were in the northern hemisphere. Figure 26 shows the global distribution of CH_3CCl_3 and a third-order polynomial fitted to it. (The nature of the polynomial is described in Table 15.) This compound shows a latitudinal distribution quite different from that of the fluorocarbons. Up to about 30°N, the CH_3CCl_3 is well mixed in the northern hemisphere with an average concentration of about 123 ppt. A fairly sharp decline seems to occur between 20°N and 20°S, and the concentration of CH_3CCl_3 then levels off to about 75 ppt.

The weighted averages of CH_3CCl_3 concentrations of about 113 ppt in the northern hemisphere and 77 ppt in the southern hemisphere best describe the burden of CH_3CCl_3 in each hemisphere. It is obvious from Figure 26 that while measurements at one point may be used to characterize the distribution of inert species, such is not the case for relatively reactive species. The reactivity of CH_3CCl_3 is clearly demonstrated by its large north-south ratio as compared to the ratio of F-11 and F-12.

While no detailed CH_3CCl_3 latitudinal profile has been available from other sources, comparison of results from Figure 26 with point measurements of Lovelock (1977) and Rasmussen et al. (1976) shows significant disagreement. These investigators have reported a much larger north-south difference than indicated by our measurements. Our results, however, are in much better agreement with the more recent measurements of Rowland (1979), Krasneck (1979) and Rasmussen (1979).

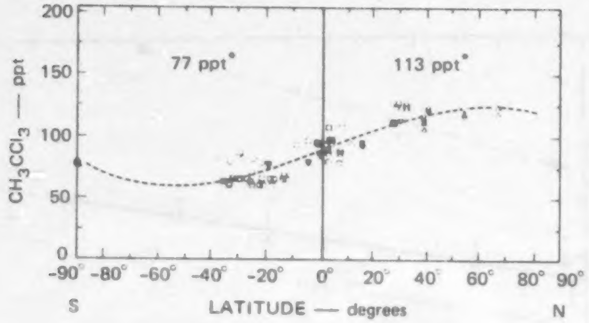


FIGURE 26 GLOBAL DISTRIBUTION OF METHYL CHLOROFORM

*Corresponds to a uniformly distributed concentration that is consistent with the measured hemispheric burden.

C. Atmospheric Growth

The dark line in Figure 27 shows the measured growth of CH_3CCl_3 during 1975 and 1978 in the northern hemisphere. These measurements were all conducted between the latitudes of 35°N to 64°N, a region where the distribution of CH_3CCl_3 is essentially uniform, as shown in Figure 26. The dashed line in Figure 27 shows the growth of CH_3CCl_3 that would result if the man-made emissions were to be distributed according to the distribution shown in Figure 26 and in the absence of any removal mechanisms. The dotted line is deduced from the dark line and indicates the global average concentration of CH_3CCl_3. The average concentration corresponds with the actual measured burden of CH_3CCl_3. This is obtained by scaling the northern temperate measured concentrations to an average global concentration according to Figure 26. A northern temperate CH_3CCl_3 concentration of 123 ppt corresponds to a northern hemisphere concentration of 113 ppt, a southern hemisphere concentration of 77 ppt, and a global average concentration of 95 ppt. Thus, the global average CH_3CCl_3 concentration is about 0.77 times the northern temperate region concentration.

It is clear from Figure 27 that the atmospheric burden of CH_3CCl_3 increased at an average rate of 15 ppt/year (≈17 percent/year) during the course of this study. The available emissions data for CH_3CCl_3 suggest an increase of about 25 ppt/year.

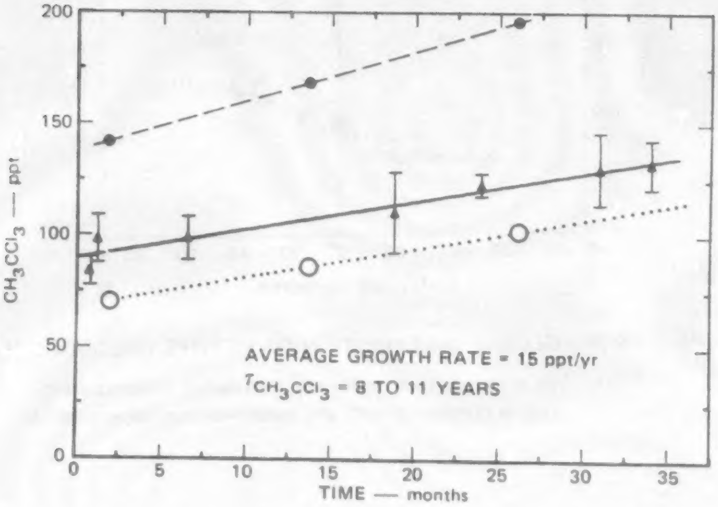


FIGURE 27 ATMOSPHERIC GROWTH OF METHYL CHLOROFORM

Time period beginning 1 November 1975

D. Sources and Sinks of Methyl Chloroform

1. Atmospheric Residence Time of Methyl Chloroform

The first interest in the residence time of methyl chloroform was generated by the qualitative possibility that CH_3CCl_3 may be used as an indicator of the HO radical abundance. During this study we soon recognized that the global budget and distribution of methyl chloroform (CH_3CCl_3) offer a unique means of determining the average HO radical concentrations in the troposphere (Singh, 1977). The uniqueness stems from three major considerations:

- Sources are entirely man-made and reliable emissions data are available.
- Reaction with HO is the major removal mechanism and the rate constant, which is accurately known (NASA, 1977) is relatively fast and not strongly dependent on temperature.
- CH_3CCl_3 is easy to measure and a relatively reliable data base is available.

The exclusively man-made sources of CH_3CCl_3 were confirmed by two observations: no natural sources are known, and measurements by Lovelock (1977) in the southern hemisphere in 1970 indicated a background CH_3CCl_3 concentration of 12 ppt consistent with man-made emissions for that period. The preliminary analysis by Singh (1977a; 1977b) clearly showed that atmospheric residence times of CH_3CCl_3 based on measurements were about a factor of 5 longer than those predicted by models. Thus, we reported that the residence time of CH_3CCl_3 was about 8 to 11 years, contrary to all earlier estimates which placed the residence time between 1 and 2 years. A longer residence time meant that CH_3CCl_3 was a potential depletor of stratospheric ozone, but even more importantly it meant that perhaps a large group of organic and inorganic chemicals resided in the atmosphere significantly longer than previously believed. However, more reliable calculations of the CH_3CCl_3 residence time had to await the data shown in Figure 26, illustrating the detailed latitudinal variation of CH_3CCl_3 that is by no means uniform.

It is clear from Figure 26 that the application of the two-box model as described by Equations 2 and 3 (Section VII-D-1) is somewhat of a simplification since the concentrations within the northern hemisphere and southern hemisphere are not uniform. The exact simulation of the global CH_3CCl_3 profile would require a two-dimensional (2-D) global model, which is currently in a state of active development. However, as will be shown in this section, valuable information is also gained by considering a two-box model. Let us define an average global residence time, τ_{ia}

$$\tau_{CH_3CCl_3} = \tau_{ia} = \frac{\left[1 + \left(\frac{N}{S}\right)\right]}{\left[\left(\frac{1}{\tau_{is}}\right) + \left(\frac{1}{\tau_{in}}\right) \cdot \left(\frac{N}{S}\right)\right]} \quad . \tag{6}$$

Solving Equations 2 and 3 for several cases makes it clear that while τ_{is} and τ_{in} are quite sensitive to the average north-south ratio of CH_3CCl_3, τ_{ia} is relatively insensitive to this ratio. Thus τ_{ia} is determined by the budget rather than by the distribution of CH_3CCl_3.

The northern temperate concentration that would result from the emitted CH_3CCl_3 if there were no removal mechanisms is also shown in Figure 27 as the dashed line. Clearly a great deal of CH_3CCl_3 has been lost to atmospheric sinks.

The application of the two-box model shows that the best estimates of $\tau_{CH_3CCl_3}$ lie between 8 and 11 years. The good agreement between measurements and project values using an 8 to 11 year residence time is shown in Figure 27. The large circles represent the global average concentration projected by models. Thus, despite the uncertainties, it is clear that the global average CH_3CCl_3 residence time is between 8 and 11 years.

Subsequent to our findings a number of other investigators have supported our results. Table 21 provides a summary of the various estimates $\tau_{CH_3CCl_3}$.

Considering all of the results reported in Table 21, it appears that the best current estimates of CH_3CCl_3 residence time lie between 6 and 12 years, excluding the outlier point from Neely and Plonka (1978). This should be compared with the CH_3CCl_3 residence time of 1.4 years reported by NAS (1976). A 6- to 12-year residence time allows 12 to 25 percent of the CH_3CCl_3 released at ground level to enter the stratosphere. This long tropospheric residence time, when coupled with the rapidly increasing emissions, suggests that CH_3CCl_3 may be a potential depleter of stratospheric O_3 in the decades ahead. Worldwide release of CH_3CCl_3 to the atmosphere currently approaches 8×10^{11}g/year and is increasing at a rate of 10 to 15 percent per year. Continued, uncontrolled release of CH_3CCl_3 to the atmosphere should be a matter of future concern.

Another somewhat less certain finding also emerges from the application of the two-box model. It appears that the residence times of CH_3CCl_3 in the northern hemisphere (τ_{in}) are significantly longer than in the southern hemisphere (τ_{is}). The ratio of τ_{in}/τ_{is}, however, is quite sensitive to the interhemispheric exchange rate (τ_e) and the northern hemisphere and southern hemisphere concentration gradient of CH_3CCl_3. Table 22 summarizes the results based on measurements by several investigators. Here we have selected the best value of τ_e to be 1.2 years. Lower values of τ_e increase the τ_{in} and τ_{is} asymmetry, while higher values tend to reduce it.

Our results from Table 21 and 22 can be summarized as follows:

$$\frac{\left(\tau_{CH_3CCl_3}\right)_{NH} + \left(\tau_{CH_3CCl_3}\right)_{SH}}{2} = \left(\tau_{CH_3CCl_3}\right)_{\text{global average}} = 8 \text{ to } 11 \text{ years,} \tag{7}$$

Table 21

METHYL-CHLOROFORM GLOBAL AVERAGE RESIDENCE TIME ($\tau_{CH_3CCl_3}$)

Estimated from Field Data	($\tau_{CH_3CCl_3}$) (Years)	Model Estimates	($\tau_{CH_3CCl_3}$) (Years)
Singh (1977)§	7 ± 1	All estimates Prior to 1977	1-3
Lovelock (1977)	5-10		
Singh (1977)§	8-11		
McConnell & Schiff (1978)	8	NAS (1976)	1.4
Chang & Penner (1978)	12	Crutzen & Fishman (1977)	10
Singh et al. (1979a)§	8-11		
Krasnec (1979)	9-12 (est)†		
Rowland (1979)	≈6 (est)†		
Neely & Plonka (1978)	3*		

*Same data as used by Lovelock (1977).

†Estimated by Singh.

§Based on data from present study.

Table 22

RESIDENCE TIMES OF METHYL CHLOROFORM IN THE NORTHERN AND SOUTHERN HEMISPHERES

Data Source	NH/SH Concentration Ratio of CH_3CCl_3	$\frac{(\tau_{CH_3CCl_3})^*_{NH}}{(\tau_{CH_3CCl_3})_{SH}}$
Lovelock (1977)	2.2	>4
Rasmussen et al. (1976)	2.2	>4
Singh et al. (1979a) Rowland (1979) Rasmussen (1979)	1.3-1.5	1.5 to 3
Krasnec (1979)	1.2	≈1

*Estimated during the present study.

$$\frac{\left(^{\tau}CH_3CCl_3\right)_{NH}}{\left(^{\tau}CH_3CCl_3\right)_{SH}} = 1.5 \text{ to } 3 \quad . \qquad (8)$$

In short we find that:

- The average global residence time of CH_3CCl_3 is significantly longer than predicted by models. Our data supports a $^{\tau}CH_3CCl_3$ value of 8 to 11 years. When estimates of other investigators are included a range of 6 to 12 years is suggested. This is a factor of 5 to 10 longer than the 1.4 year $^{\tau}CH_3CCl_3$ values reported by NAS (1976).
- A 6 to 12 year $^{\tau}CH_3CCl_3$ allows an estimated 12 to 25 percent of all CH_3CCl_3 to enter the stratosphere. The long tropospheric residence time, when coupled with the rapidly increasing emissions, suggests that CH_3CCl_3 may be a potential depletor of stratospheric O_3 in the decades ahead. The impact may be further escalated in the future as more and more nations substitute CH_3CCl_3 to replace the declining usage of C_2HCl_3 and to some extent C_2Cl_4 (for toxicity and health reasons), thereby resulting in extraordinary increases in CH_3CCl_3 emissions. Worldwide release of CH_3CCl_3 to the atmosphere currently approaches 7 x 10^{11}g/year and is increasing at a rate of 10 to 15 percent per year. Continued uncontrolled release of CH_3CCl_3 to the atmosphere should be a matter of future concern.
- The residence time of CH_3CCl_3 appears to be longer in the northern hemisphere when compared to the southern hemisphere.

2. Methyl Chloroform as an Indicator of the Hydroxyl Radical Abundance in the Northern and Southern Hemispheres

As stated earlier the major removal mechanism for CH_3CCl_3 is expected to be reaction with the hydroxyl radical (HO). The rate constant of CH_3CCl_3 + HO is well known ($K = 3.5 \times 10^{-12} \exp(-1562/T)$ cm^3/molecule/sec), the residence time of CH_3CCl_3 is significantly long, and the tropospheric reservoir sufficiently large that short-term perturbations in global emissions are unlikely to alter significantly the distribution of CH_3CCl_3. Therefore, the residence time of CH_3CCl_3 could be used to determine average hydroxyl radical concentrations. Once the average HO abundance is determined, the residence times of a vast number of chemicals can be determined.

In the past, the HO abundance has been derived from 1-D models which have never been satisfactorily validated. The uncertainty in these models allows for an uncertainty in the HO abundance of a factor of 10 or more (Isaksen and Crutzen, 1977). Therefore, the HO estimates from CH_3CCl_3 residence time data should be used to validate existing models (Crutzen and Fishman, 1977).

Using the rate constant for the CH_3CCl_3 + HO reaction at a weighted-average tropospheric temperature of 265°K ($k = 9.64 \times 10^{-15}$ $cm^3 \cdot$molec/sec) we can calculate the HO burden from CH_3CCl_3 residence times given in Equations 7 and 8.

$$(\overline{HO})_{\text{global average}} = \frac{(\overline{HO})_{NH} + (\overline{HO})_{SH}}{2} = 3 \text{ to } 4 \times 10^5 \text{ molec/cm}^3 \ ,$$

$$\frac{(\overline{HO})_{SH}}{(\overline{HO})_{NH}} = 1.5 \text{ to } 3 \ . \qquad (9)$$

The global average HO abundance of 3 to 4 × 10^5 molec/cm^3 is a factor of 5 to 10 lower than the values estimated by many modelers (Weinstock et al., 1979). More recently, Crutzen and Fishman (1977) have revised their photochemical model to conform with these inferred HO values.

The significance of reduced HO levels cannot be overemphasized, since it is a major tropospheric loss mechanism for a majority of hydrocarbons and halocarbons. A five-fold increase in the lifetime of these trace constituents is likely to increase substantially the estimates of stratospheric chlorine contribution due to F-22, CH_3CCl_3, CH_2Cl_2, etc., as well as result in an increased intrusion of nonmethane hydrocarbons (such as C_2H_6, C_3H_8, and C_2H_2) which have been all but ignored in existing models. The high activation energy of the C_2H_6 + HO reaction rate (3600 cal/mole) also permits a long lifetime at the reduced temperatures of the lower stratosphere. In addition, the rate constant for the C_2H_6 + Cl reaction is about 1000 times faster than for CH_4 + Cl and a small fraction of C_2H_6 could produce an important competing reaction. These factors could change the estimates of stratospheric ozone losses. Methane oxidation reactions, proposed to control the tropospheric O_3 and CO distribution, would be impacted by these considerations. Reduced HO levels further help to resolve the current discrepancies in the tropospheric budget and distribution of CO.

Although some differences in the northern hemisphere and southern hemisphere levels of HO are to be expected because of natural differences in water vapor, ozone, and particulate concentrations, a much larger difference can be attributed, at least in part, to CO (a principal sink for HO) whose levels are three times higher in the northern hemisphere when compared with the southern hemisphere (Seiler, 1974). If the additional CO in the northern hemisphere is predominantly from man-made sources, as the current data seem to suggest, continued release of CO has and will further reduce the HO levels, thereby depleting the scavenging ability of the atmosphere. Additional dependence on fossil fuels in coming years is likely to cause more severe depletions in the HO abundance. These HO losses will not only allow a larger stratospheric input of anthropogenic halocarbons and hydrocarbons, but may already have altered the stratospheric chemistry by permitting increased intrusion of natural ubiquitous tropospheric species, such as CH_4 and CH_3Cl. We wish to add, however, that the possibility of a natural hemispheric CO (and HO) gradient from unknown CO sources in the northern hemisphere, although unlikely, cannot be completely ruled out at this time.

E. Discussion of Results

The major results of this section can be summarized as follows:

- Contrary to previous belief the observational data best supports an atmospheric residence time for CH_3CCl_3 of 8 to 11 years. This allows about 15 to 22 percent of all CH_3CCl_3 released at ground level to enter the stratosphere. The long residence time and the rapid growth of CH_3CCl_3 cause it to be a potential depletor of stratospheric ozone.
- Methyl chloroform appears to have excellent properties to act as an indicator of seasonally average hydroxyl radical concentration. Our data suggests a global average HO concentration of 3 to 4 × 10^5 molec/cm^3. When data by other investigators is included an HO concentration range of 3 to 6 × 10^5 molec/cm^3 can be calculated.
- The distribution of CH_3CCl_3 in the northern hemisphere and southern hemisphere points to an asymmetric HO distribution with higher average HO levels in the SH($^{(HO)}$SH/$(HO)_{NH} \geq 1.5$). The uncertainty in this result is larger because of limited data and greater sensitivity of calculations. The conclusion is qualitatively justifiable and can be attributed to carbon monoxide (a principle sink for HO) and its asymmetric hemispheric distribution. More data is required to confirm these findings.

SECTION 11

ATMOSPHERIC METHYL CHLORIDE

A. Global Emissions

Table 23 shows the estimated emissions of CH_3Cl from man-made sources. The accuracy of this data is not expected to be better than a factor of two.

Table 23

GLOBAL ATMOSPHERIC RELEASE OF METHYL CHLORIDE
(in 10^6 kg/yr)

Year	Methyl Chloride Release
1955	0.5
1956	0.6
1957	0.7
1958	0.6
1959	1.0
1960	1.2
1961	1.5
1962	1.6
1963	1.7
1964	1.9
1965	2.7
1966	3.4
1967	4.0
1968	4.4
1969	5.9
1970	6.1
1971	6.3
1972	6.6
1973	7.9
1974	6.7
1975	5.3
1976	5.5
1977	6.0
Total	82.1

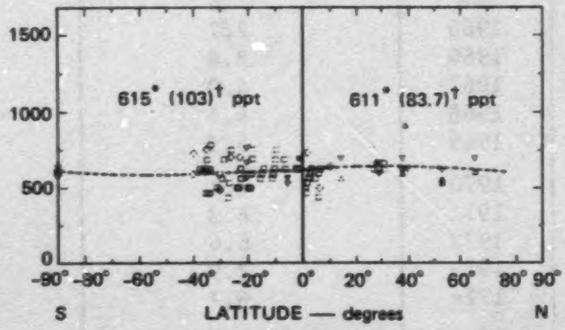
Source: Bauer (1978)

However, for the purposes of the present discussion the emissions data serve a qualitatively useful purpose. It is clear from Table 23 that the total release of CH_3Cl has been about 0.082 million tons. An upper limit of 0.16 can be estimated. If all of the 0.16 million tons were to be uniformly distributed in the troposphere, an average global concentration of less than 20 ppt would result. In actuality, since CH_3Cl is rather rapidly removed, the emissions from Table 23 could not lead to an atmospheric concentration of more than 4 ppt. It suffices to say that man-made emissions of CH_3Cl have been quite small.

B. Global Burden and Distribution

A number of investigators have measured CH_3Cl in the northern hemisphere and background concentrations have varied between 400 and 1500 ppt (Lovelock, 1975; Grimsrud and Rasmussen, 1975, Singh et al., 1977a, 1977c). All measurements indicated a large burden of CH_3Cl that could not be accounted for by man-made sources, which appear to be quite small.

Figure 28 shows the global distribution of CH_3Cl as measured by us. It is clear from Figure 28 that CH_3Cl is essentially uniformly distributed over the globe. Since no other profile of the global distribution of CH_3Cl has been published, comparisons with other investigators are not possible.



*Average hemispheric concentration

†Standard deviation

FIGURE 28 GLOBAL DISTRIBUTION OF METHYL CHLORIDE

It is obvious from Figure 28 that CH_3Cl has an average global background concentration of about 615 ppt. Unlike CH_3CCl_3, there is no north-south gradient for CH_3Cl, despite the fact that CH_3Cl is at least 2 to 3 times more reactive than CH_3CCl_3 (see Section XVI). This only points to a very large natural source of CH_3Cl that is relatively uniformly distributed.

It is also interesting to note that CH_3Cl shows a large atmospheric variability with a standard deviation of about 15 percent. Within the northern hemisphere we have observed higher values in the Pacific marine environment that fall off as we enter deep into continental atmospheric areas. Table 24 shows the variability of CH_3Cl as measured at clean continental and marine environments.

Table 24 shows the lowest CH_3Cl concentration of 586 ppt at Site 12, which is a truly continental surface site at about 800 m above sea level. The corresponding concentration at the marine Site 11 in roughly the same season is 730 ppt. It further appears that a seasonal gradient in CH_3Cl levels exists, with higher concentrations in spring or early summer. A comparison of data from Sites 11 and 14, which are identical for all practical purposes, indicates CH_3Cl levels that are about 15 percent lower in September when compared to May. The data base, however, is too sparse to generalize these observations. It is adequate to say that CH_3Cl must have large natural sources. These natural sources give it a complex atmospheric variability that cannot be adequately characterized with the limited existing data. Our atmospheric measurements over the continental United States appeared to indicate an oceanic source of CH_3Cl. Indeed, the highest concentrations of CH_3Cl in the clean environments approaching 2 ppb were measured by us in the marine boundary layer. This in no way implies that other natural or secondary man-made sources of CH_3Cl do not exist. Here it is pertinent to add that in urban areas we have found significantly higher levels of CH_3Cl indicating as yet unknown sources associated with man-made activities.

C. The Oceanic Source

As suggested by our field measurements, a preliminary attempt was made to measure CH_3Cl in Pacific seawater. These measurements are shown in Table 17.

Table 24

AVERAGE CONCENTRATIONS OF SELECTED TRACE CONSTITUENTS IN CLEAN ENVIRONMENTS

Chemicals	Site 5 High Altitude Continental (May 1976)	Site 11 Surface-Marine (May 1977)	Site 12 Surface Continental (June 1978)	Site 14 Surface-Marine (Sept. 1979)	Hemispheric Averages (Nov.-Dec. 1977)	
					Northern Hemisphere	Southern Hemisphere
CCl_2F_2 (ppt)	204 (19)†	220 (20)	253 (17)	252 (16)	230 (26)	210 (25)
CCl_3F (ppt)	116 (5)	126 (13)	138 (6)	152 (19)	133 (13)	119 (12)
$CHClF_2$ (ppt)	--	20-30	20-40	—	--	--
$CHCl_2F$ (ppt)	14 (4)	5 (2)	6 (1)	7 (1)	5 (3)	4 (1)
CCl_2FCClF_2 (ppt)	20 (3)	23 (6)	23 (5)	22 (2)	19 (4)	18 (3)
$CClF_2CClF_2$ (ppt)	—	12 (5)	12 (3)	13 (3)	12 (2)	10 (1)
SF_6 (ppt)	0.23 (0.03)	0.26 (0.04)	0.39 (0.06)	0.30 (0.14)	0.31 (0.04)	0.27 (0.01)
CCl_4 (ppt)	114 (6)	123 (8)	128 (12)	125 (8)	122 (5)	119 (4)
$CHCl_3$ (ppt)	17 (2)	20 (5)	16 (5)	—	14 (7)	≤3
CH_2Cl_2 (ppt)	—	45 (22)	54 (15)	39 (17)	44 (14)	20 (4)
CH_3Cl (ppt)	713 (51)	730 (134)	586 (64)	628 (50)	611 (84)	615 (103)
CH_3I (ppt)	9 (5)	5 (3)	2 (1)	--	2 (1)	2 (1)
CH_3Br (ppt)	5 (3)	20 (6)	5 (1)	13 (5)	--	—
CCl_3CCl_3 (ppt)	—	7 (1)	6 (2)	—	--	—
CH_3CCl_3 (ppt)	103 (9)	111 (18)	130 (16)	132 (11)	113‡	77
CH_2BrCH_2Br (ppt)	—	5 (1)	≤5	≤5	--	—
CCl_2CCl_2 (ppt)	31 (10)	34 (5)	41 (10)	34 (11)	40 (12)	12 (3)
$CHClCCl_2$ (ppt)	15 (3)	11 (1)	13 (4)	17 (7)	16 (8)	<3
$COCl_2$ (ppt)	22 (5)	15 (4)	—	15 (5)	--	--
N_2O (ppb)	312 (18)	313 (8)	311 (5)	312 (6)	311 (2)	311 (3)
NO (ppb)	1.3 (0.9)	<5.0	1 (2)	3 (3)	--	--
NO_2 (ppb)	4.0 (1.3)	<5.0	3 (2)	8 (5)	--	--
$CH_3(CO)OONO_2$, PAN (ppt)	--	100 (55)	252 (103)	80 (57)	--	--
$CH_3CH_2(CO)OONO_2$, PPN (ppt)	--	40 (17)	--	--	--	--
O_3 (ppb)	53 (12)	35 (5)	31 (11)	--	--	--
CO (ppb)	—	118 (15)	175 (50)	--	--	--
CH_4 (ppb)	1412 (103)	1479 (19)	1600 (80)	1563 (284)	1430 (5)	1390 (51)
C_2H_2 (ppt)	--	<400	--	<200	<200	<200
C_2H_6 (ppt)	--	1951 (281)	9980 (4950)	1595 (986)	1060‡	524 (15)

ppt = 10^{-12} v/v; ppb = 10^{-9} v/v

†Standard deviation in parentheses.

‡Nonuniform concentration within each hemisphere, the average represents that concentration in the hemisphere which would result if the hemispheric mass of the species were to be uniformly distributed.

It is clear from Table 17 that the surface concentration of CH_3Cl in the Pacific is quite variable, with values somewhat higher near the equator. The average surface concentration found was 26.8 ng/liter. Using an S_{CH3Cl} of 2.65 (Dilling, 1971), $D = 10^{-5}$ cm^2/sec, and $Z = 90 \mu m$, the simple film-diffusion model described in Equation 4 can be used to estimate an oceanic flux. Using Equation 4 and other parameters described above, we calculated CH_3Cl flux from ocean to the atmosphere of 2.6×10^{-14} g cm^{-2}/sec. Extending this to the world ocean body gives an exchange rate of 3.0×10^{12} g/year. From our measurements, the atmospheric burden of CH_3Cl can be estimated to be 5.5×10^{12} g. Thus, on the basis of our limited data, the ocean appears to be a significant source of CH_3Cl, which can provide an atmospheric turnover rate of about 2 years. This is in reasonable agreement with the estimated CH_3Cl residence time of about 2 to 3 years because of attack ($HO = 3 \times 10^5$ to 5×10^5 moleulces/cm^3). Although the data base is too scarce and variable to make a strong case, it may turn out that CH_3Cl atmospheric burden is dominated by the oceanic source. It should be pointed out that microbial fermentation and combustion of vegetation as sources of CH_3Cl have also been proposed (Palmer, 1976) but remain largely unquantified. The mechanism by which CH_3Cl may be produced in the ocean is unclear but reactions involving CH_3I and the chloride ion of seawater have been suggested as a possible source of oceanic CH_3Cl (Zafiriou, 1975).

D. Residence Time of CH_3Cl

The residence time of CH_3Cl can be estimated in two principal ways: by atmospheric variability of CH_3Cl and removal via reaction with HO.

It is clear from Figure 28 that CH_3Cl is relatively uniformly distributed and a variability of about 15 percent (σ_t) is associated with its global distribution. We estimate that on the average about 7 percent of this variability (σp) is associated with analytical methodology. Thus, the true atmospheric variability of CH_3Cl can be estimated to be about 13 percent ($\sigma_a^2 = \sigma_t^2 - \sigma_p{}^2$). For species with a uniform source distribution, the approximate statistical relationship of Junge (1974) can be used:

$$\tau_{CH_3Cl} = \frac{14}{\sigma_a(\%)} \approx 1.1 \text{ year} \quad .$$

Since the above relationship is accurate to within a factor of 3, we estimate a CH_3Cl atmospheric residence time of 1 to 3 years. The upper limit of this estimate is probably more correct since σ_t of 15 percent is partially high because of the proximity of our measurements to the oceanic source. The best estimate of average HO derived by us from the CH_3CCl_3 data is 3 to 4 × 10^5 molecules/cm^3. From the known reaction rate of CH_3Cl with HO (see Section XVI) we estimate that CH_3Cl would have a mean residence time of 2.5 to 3.5 years.

Thus, two completely independent estimates of τ_{CH_3Cl} are in good agreement and point to an estimated τ_{CH_3Cl} of 2 to 3 years.

E. Discussion of Results

Unlike other halocarbons we measured, CH_3Cl is the only one with a large natural source. The atmospheric abundance as well as the relatively uniform global distribution of CH_3Cl (despite its high reactivity) point to the existence of large natural sources. Our limited data support the conclusion that one of the most significant natural sources of CH_3Cl is the ocean. This oceanic source is estimated to be 3 million tons/year and can account for nearly all of the atmospheric burden of CH_3Cl. The possibility that unknown man-made sources yet remain to be quantified also exists. It is unlikely, however, that these would be comparable to the natural sources in quantity. Atmospheric variability data as well as the removal by hydroxyl radical point to a 2- to 3-year tropospheric residence time. Thus, less than 6 percent of all the CH_3Cl released at ground level will enter the stratosphere. The mechanisms by which CH_3Cl is produced in the ocean are not understood, and the distribution of CH_3Cl in the ocean is highly variable and poorly characterized.

SECTION 12

CHLOROFORM, METHYLENE CHLORIDE, TRICHLOROETHYLENE, TETRACHLOROETHYLENE, HEXACHLOROETHANE AND PHOSGENE

A. Global Emissions

The estimated global emissions of the first four chemicals ($CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4) are listed in Table 25. These data are estimated from production figures and usage patterns. The accuracy of this data is probably better than ±50%.

Table 25

GLOBAL ATMOSPHERIC RELEASE OF CHLOROFORM, METHYLENE CHLORIDE, TRICHLOROETHYLENE AND TETRACHLOROETHYLENE (in 10^6 kg)

Year	Chloroform	Methylene Chloride	Trichlor-ethylene	Tetrachlor-ethylene
1955	2	49	453	154
1956	3	63	496	160
1957	3	63	485	170
1958	2	59	423	161
1959	4	75	516	175
1960	4	75	506	180
1961	4	77	443	194
1962	5	96	511	276
1963	5	99	528	280
1964	6	119	531	316
1965	8	141	624	370
1966	9	178	689	400
1967	9	175	703	460
1968	9	202	744	549
1969	11	244	856	548
1970	12	268	877	610
1971	11	267	738	608
1972	12	314	613	633
1973	12	346	648	609
1974	15	394	622	630
1975	13	331	420	586
1976	14	356	453	577
1977	15	375	435	570
Total	188	4,366	13,304	9,216

Source: Bauer (1978)

Hexachloroethane is not manufactured in large quantities in the United States and only 500 tons/year are imported from Europe. Most of the C_2Cl_6 produced is released to the atmosphere. Since the molecule is very stable, it may tend to accumulate in the atmosphere. Thus, the emissions of C_2Cl_6 as a small impurity in C_2Cl_4 may be one of the sources. No global emissions inventory is currently available.

Phosgene is predominantly manufactured for captive use and very little direct release takes place. Table 26 shows that even though the production of phosgene has been significant, the sales have never exceeded 6 million kg/year. While the release of phosgene may create a local health hazard, there is no evidence to support the assumption that the direct emissions of phosgene are large. The major source of phosgene in the atmosphere is likely to be from the photooxidation of chloroethylenes (Singh, 1976). This secondary source is difficult to quantify accurately but may be as large as 0.3 million tons/year (Singh, 1976).

Table 26

PHOSGENE PRODUCTION, SALES, AND RELEASE IN THE UNITED STATES (in 10^6 kg)

Year	Production	Sales	Emissions
1957	2.4	2 to 6	negligible
1958	4.1		
1959	16.7		
1960	16.6		
1961	26.3		
1962	50.9		
1963	96.4		
1964	111.4		
1965	129.4		
1966	149.9		
1967	169.1		
1968	203.0		
1969	229.5		
1970	280.7		
1971	241.2		
1972	289.5		
1973	331.0		

Source: CIS (1979)

B. Atmospheric Measurements

1. Chloroform

There is little doubt that large man-made sources of chloroform exist. Table 24 shows a typical background concentration at northern temperate latitudes of 16 to 20 ppt. The northern hemisphere average, as determined from an analysis of a limited number of samples, was found to be 14 ± 7 ppt. We suspect that the background concentration of $CHCl_3$ is latitude-dependent and is unlikely to be uniform in the northern hemisphere. In the southern hemisphere $CHCl_3$ was barely detectable and a background concentration of ≤ 3 ppt was reported. A small gradient away from the marine environment was observed. This gradient cannot be easily attributed to natural oceanic sources of $CHCl_3$. As will be discussed in Section XVII, the Pacific coastal waters appeared to be significantly contaminated with $CHCl_3$ and may have caused this apparent marine air/continental air concentration gradient.

2. Methylene Chloride

Methylene chloride is a well-known solvent and is released in significant quantities. Over the northern hemisphere average background concentrations in the range of 40 to 55 ppt have been measured (Table 24). The northern hemisphere background concentration in 1977 was measured to be 44 ± 14 ppt. The southern hemisphere average concentration was 20 ± 4 ppt. Thus, a significant north-south gradient is apparent. The emissions of CH_2Cl_2 from man-made sources alone (Table 25), when coupled with 1-year atmospheric residence time (see Section XVI), are consistent with the measured atmospheric global burden. A short average residence time of the order of 1 year can cause the atmospheric abundance of CH_2Cl_2 to vary seasonally. Superimposed on this variation is the variability in emissions. Additional data is required to characterize more adequately the abundance and variability of these relatively short-lived species.

3. Trichloroethylene and Tetrachloroethylene

Despite the high emission strength of these species, as suggested by data in Table 25, the background concentrations of these species were quite low. Table 24 clearly shows an average northern hemisphere background concentration for C_2Cl_4 of about 40 ppt. Between 1975 and 1978 they have typically varied between 30 and 40 ppt. Table 24 also shows that the southern hemisphere C_2Cl_4 abundance is about a third of its northern hemisphere value. No global distribution profile is available but significant latitudinal gradients can be expected. These gradients are expected to be even larger for C_2HCl_3. The northern hemisphere average of 11 to 17 ppt for $C_2H\ Cl_3$ can be compared to a southern hemisphere value of less than 3 ppt. The low background concentrations of C_2Cl_4 and C_2HCl_3 as well as the large northern hemisphere and southern hemisphere gradients are indicative of short residence times.

4. Hexachloroethane

As stated earlier, C_2Cl_6 is not directly emitted in large quantities. Typical background concentrations have varied between 5 and 7 ppt. C_2Cl_6 measurements in the northern hemisphere are highly limited and are not available from any source other than our own. No southern hemisphere data is available.

5. Phosgene

Phosgene was measured for the first time at several clean sites at concentrations of about 15 ppt. As is clear from Table 26, the direct emissions of phosgene are very small. No measurements in the free troposphere and the southern hemisphere are currently available.

C. Discussion of Results: Sources and Sinks

The total emissions of $CHCl_3$ from man-made activities are estimated to be 0.2 million tons. The accuracy of this estimate is low. $CHCl_3$ is relatively rapidly removed from the atmosphere via reaction with HO and a residence time of about 1 year is estimated (Section XVI) No natural sources of $CHCl_3$ are known, and the northern hemisphere and southern hemisphere gradient further suggests that these sources, if they exist, are not uniformly distributed. There is little doubt that dominant emissions of $CHCl_3$ occur in the northern hemisphere. If the measured concentration of $CHCl_3$ is representative of the northern hemisphere troposphere, then emissions data in Table 25 must be a gross underestimate. It is also possible that secondary anthropogenic sources of $CHCl_3$ (such as chlorination of water) exist. These sources have not yet been quantified.

The atmospheric fate of CH_2Cl_2 is similar to $CHCl_3$ and it also persists in the atmosphere for about 1 year (see Section XVI). Unlike $CHCl_3$, an estimated 4.2 million tons of CH_2Cl_2 have been released to the atmosphere (Table 25). Because of its increasing use in solvent applications, its growth has been rapid. In 1965 the emissions of CH_2Cl_2 were 25 percent of those of C_2HCl_3. In 1977 this fraction had increased to 85 percent. The measured concentration of 40 to 50 ppt in the northern hemisphere and about 20 ppt in the southern hemisphere are not inconsistent with the available emissions data. There is little doubt that essentially all CH_2Cl_2 is of man-made origin. It is useful to add that CH_2Cl_2, in a manner similar to CH_3CCl_3, could be used as an indicator of HO radical abundance. Because of its relatively short residence time of one year, a better resolution of the emissions data would be needed. The advantage of CH_2Cl_2 would be its greater reactivity which could potentially be used to establish seasonal trends in the HO abundance.

Both C_2HCl_3 and C_2Cl_4 have been large volume chemicals. These have been in disfavor in recent years, largely for toxicity reasons, but also because of their photochemical involvement with other hydrocarbons in smog formation processes. To date an estimated 13 million tons of C_2HCl_3 and 9 million tons of C_2Cl_4 have been released to the atmosphere. There is no doubt that both these chemicals are exclusively of man-made origin and at least 95 percent of their release occurs in the northern hemisphere. The southern hemisphere data is virtually nonexistent but our limited measurements are consistent with man-made sources in the northern hemisphere. The northern hemisphere background concentration of 30 to 40 ppt of C_2Cl_4 is in agreement with a man-made source and a residence time of 0.8 years (see Section XVI). On the other hand, C_2HCl_3 is highly reactive, and the measured background concentration of about 15 ppt is higher than can be explained from emissions data. The measurements of Cronn et al. (1976) suggest few vertical gradients in the troposphere for species with residence times of greater than a few months. For C_2HCl_3, however, the residence time is estimated to be only about 2 weeks (Section XVI) and significant vertical gradients can be expected. Thus, the ground-level measured background concentration of a very short-lived species such as C_2HCl_3

may not be representative of the entire troposphere. The data of Cronn et al. (1976) showing virtually no vertical gradients for C_2HCl_3 probably suffers from contamination problems.

The sources of C_2Cl_6 are not known well enough to assess its source-sink relationship. C_2Cl_6 can be expected to be essentially inert in the troposphere. It is possible, however, that it may eventually accumulate in marine biota. The possibility exists that C_2Cl_6 abundance represents an accumulation of emissions that have occurred over a period of many years. This opens up the possibility that it may be present or may have been present as an impurity in a high-volume chemical such as C_2HCl_3 or C_2Cl_4.

The sources and sinks of phosgene have already been discussed (Singh, 1976; Singh et al., 1977c). We concluded that the direct primary emissions of $COCl_2$ are negligible. Its major source is atmospheric photooxidation of C_2HCl_3 and C_2Cl_4. The major sinks appear to be liquid-phase hydrolysis or heterogeneous decomposition on surfaces. Gas-phase hydrolysis was found to be a negligible sink. The reaction rate of $COCl_2$ with HO has not yet been measured. In any case, it appears that $COCl_2$ residence time is of the order of several months.

SECTION 13

ATMOSPHERIC BROMINE AND IODINE SPECIES

Only two brominated organics have been identified in the lower troposphere. These are ethylene dibromide and methyl bromide. The concentrations of both these species are low and variable. Their tropospheric distribution remains poorly characterized.

Table 27 provides estimates of the worldwide production and release of CH_2BrCH_2Br and CH_3Br. A great deal of CH_2BrCH_2Br is used in gasoline but is converted to particulate matter (largely $PbBr_2$) that is lost to the ground via dry and wet deposition processes. One can only roughly estimate that between 5 and 25 percent of CH_2BrCH_2Br escapes to the atmosphere. Table 27 clearly shows that this source of bromine can be between 15 and 75 million kg(Br)/year.

Table 27 also shows the production data for CH_3Br. It is clear from this table that the production of CH_3Br is much smaller than CH_2BrCH_2Br. However, most of CH_3Br is used as a soil fumigant and a significant fraction is released to the atmosphere. We estimate that 50 to 75 percent of all CH_3Br manufactured is released to the atmosphere. Thus, a man-made bromine source of 13 to 20 million kg (Br)/year is attributable to CH_3Br. Together, CH_2BrCH_2Br and CH_3Br add up to a man-made source of 28 to 95 million kg (Br)/year. Other forms of organic bromine probably exist. $CHBr_3$ has been identified to be present in drinking water. Fluorocarbon-13B1 ($CBrF_3$) is a commonly used and an increasingly popular fire extinguisher. It is also used as a common tracer in scientific studies. Among the various brominated species, $CBrF_3$ is the only one that is likely to enter the stratosphere essentially intact. The current production of $CBrF_3$ is too small to be of any consequence.

The only organic iodine species to have been identified in the atmosphere is CH_3I. No significant man-made sources of CH_3I are known to exist.

The global distribution of CH_2BrCH_2Br and CH_3Br has not been characterized. Indeed no atmospheric data from the southern hemisphere is available. No

Table 27

ESTIMATED WORLD-WIDE PRODUCTION AND RELEASE OF ETHYLENE DIBROMIDE AND METHYL BROMIDE

(in units of 10^6 Kg)

Year	Ethylene Dibromide[*]		Methyl Bromide	
	Production	Release	Production	Release
1955	120	5 to 25% of Production	--	
1956	127		--	
1957	124		--	
1958	121		--	
1959	126		--	
1960	108		--	
1961	112		--	
1962	116		--	
1963	121		--	
1964	144		--	
1965	170		9	50 to 75% of Production
1966	164		10	
1967	173		12	
1968	178		13	
1969	191		12	
1970	189		14	
1971	181		14	
1972	205		16	
1973	217		19	
1974	192		20	
1975	174		23	
1976	150[†]		26	
Total 1955-1976	3380		188	

[*] Based on U.S. data (CIS, 1979). U.S. Production is taken to be 75 percent of world production between 1955 and 1969 and 70 percent between 1970 and 1976.

[†] For the year 1976 it is assumed that the production outside U.S. was the same as in 1975.

measurements other than our own have been published even for the northern hemisphere. Table 24 clearly shows that the surface background concentration of CH_2BrCH_2Br is less than 5 ppt. The corresponding concentrations for CH_3Br are highly variable. In May 1977 a mean concentration of 20 ppt was measured at a marine site in Point Arena (Site 11). At locations away from the marine environment (Sites 5 and 12) and in about the same season, average concentrations of 5 ppt were measured (Table 24). In September 1979 at a location identical to Site 11 (Site 14) the average of measured CH_3Br concentrations was about 13 ppt. Briefly then, the data from Table 24 suggest higher values of CH_3Br in the marine air compared to continental air and a possible seasonal variation of CH_3Br in the marine air.

Preliminary measurements of Lovelock (1975) in coastal water provide further support for the oceanic source of CH_3Br. No measurements for the open oceans are available.

It is clear from Table 24 that the concentration of CH_3I in the marine environment typically varies between 1 and 5 ppt and has an average value of about 2 ppt. CH_3I seems to be of oceanic origin. Limited coastal water samples from the California coastal waters were found to contain about 50 ppt of CH_3I in helium in equilibrium with water (Singh, et al., 1977c). Lovelock (1973; 1975) has measured CH_3I concentrations in excess of 100 ppt in coastal waters elsewhere. Ambient values as high as 61 ppt were measured at Site 2 during a thunderstorm. It is likely that the ocean spray provides a localized source of CH_3I during turbulent conditions. Because of the high reactivity of CH_3I found in past analyses, its atmospheric residence is limited to about 3 days. No measurements of CH_3I from the free troposphere are available. The northern hemisphere and southern hemisphere marine levels are essentially indistinguishable.

On the whole, the atmospheric distribution of both brominated and iodated organics has not yet been satisfactorily characterized. Additional research in this area is clearly needed.

SECTION 14

GLOBAL BUDGETS OF ORGANIC CHLORINE, BROMINE, IODINE, AND FLUORINE

Because of continual release of pollutants into the atmosphere, the halogen budget is a constantly changing quantity. In its present condition the atmospheric halogen burden is sufficiently large that yearly perturbations are not expected to alter it by more than 5 to 10 percent. Table 28 lists the concentrations of a large number of chemical species that we measured at the end of 1977. We choose this period because it is the only period for which we have both northern hemisphere and southern hemisphere data. The major sources of species are also defined in Table 28.

Table 29 uses the data from Table 5 to develop a Cl, Br, I, and F budget for the northern hemisphere, southern hemisphere and globe. In addition, the contributions from man-made and natural sources are defined.

It is clear from Table 29 that the global average Cl budget at the end of 1977 was 2.7 ppb while that in the northern hemisphere was 2.9 ppb. This implies that the odd chlorine available in the stratosphere could not exceed 3 ppb. The possibility that other, as yet unquantified, chlorinated species exist in the troposphere cannot be completely dismissed. However, measurements of total organic chlorine, as measured by Berg and Winchester (1976), show relatively good agreement with our results and do not support the existence of large unknown organic chlorine sources. We further calculate from the source categories shown in Table 28 that 77 percent of the tropospheric organic chlorine is man-made while the remaining 23 percent is of natural origin. Thus a significant perturbation of the natural atmosphere from man-made activities has already taken place.

Anderson (1979) has measured free chlorine concentrations in the stratosphere and reports maximum levels at about 40 kms that vary between 1 to 2 ppb in late 1977. In one flight a maximum of 7 ppb is measured. This latter value would be in serious disagreement with our findings that indicate an upper limit of 3 ppb of total odd free chlorine.

Table 28

AVERAGE BACKGROUND CONCENTRATIONS OF IMPORTANT TRACE CONSTITUENTS

Compound	Major[†] Source	Concentration*		
		Northern Hemisphere Average	Southern Hemisphere Average	Global Average
N_2O	N	311 ppb	311 ppb	311 ppb
CCl_2F_2 (F-12)	A	230 ppt	210 ppt	220 ppt
CCl_3F (F-11)	A	133 ppt	119 ppt	126 ppt
CCl_2FCClF_2 (F-113)	A	19 ppt	18 ppt	18 ppt
$CClF_2CClF_2$ (F-114)	A	12 ppt	10 ppt	11 ppt
$CHClF_2$ (F-22)	A	20-30 ppt	--	--
$CHCl_2F$ (F-21)	A	5 ppt	4 ppt	4 ppt
SF_6	A	0.31 ppt	0.27 ppt	0.29 ppt
CCl_4	A	122 ppt	119 ppt	120 ppt
CH_3CCl_3	A	113 ppt	77 ppt	95 ppt
CH_3Cl	N	611 ppt	615 ppt	613 ppt
CH_3I	N	2 ppt	2 ppt	2 ppt
CH_3Br	A, N	5-20 ppt	--	--
$CHCl_3$	A	14 ppt	≤3 ppt	8 ppt
CH_2Cl_2	A	44 ppt	20 ppt	32 ppt
C_2HCl_3	A	16 ppt	<3 ppt	8 ppt
C_2Cl_4	A	40 ppt	12 ppt	26 ppt
C_2Cl_6	A	≤5 ppt	--	--
CH_2BrCH_2Br	A	≤5 ppt	--	--
CH_4	N, A	1430 ppb	1390 ppb	1410 ppb
C_2H_6	N, A	1060 ppt	524 ppt	792 ppt
C_2H_2	A	<200 ppt	<200 ppt	<200 ppt

*For those species where significant latitudinal variations within the hemisphere were observed, the average concentration within each hemisphere is the concentration that, when uniformly mixed in the hemisphere, represents the total burden of the species in that hemisphere. The concentration data are for late 1977: ppt = 10^{-12} v/v; ppb = 10^{-9} v/v.

[†] N = Natural; A = Anthropogenic.

The organic bromine and iodine budgets are much less certain. In the case of bromine, the only measurements available were taken during the conduct of this study. The only two brominated species that we measured are CH_3Br and CH_2BrCH_2Br. However, even for these species the data are very scarce. A preliminary interpretation suggests an organic Br content of 10 to 30 ppt in the northern hemisphere, of which 50 to 90 percent may be of natural origin (Table 29). No data from the southern hemisphere are available.

There do not appear to be any significant sources of organic iodine. The only species identified to date is methyl iodine, which is present at an average concentration of 2 to 5 ppt in the marine boundary layer. The mean tropospheric concentration is expected to be much less than 2 ppt because of the high reactivity of CH_3I. Nearly all of CH_3I is of natural origin (Table 29).

Table 29 also shows that there is about 1 ppb of F and almost all of it is attributable to man-made sources. In developing the F budget we have added the contribution from CF_4, which is present at a concentration of about 65 ppt (Rasmussen et al., 1979) but was not measured during this study.

Thus it appears that nature contributes virtually no organic fluorine and nearly all of the iodine to the troposphere. It is pertinent to add that sources and abundance of Br and I may be poorly characterized and as yet unknown species may be present. Special emphasis is needed to undertake the identification of new bromine and iodine species and better characterization of those already measured.

Table 29

TROPOSPHERIC CHLORINE, BROMINE, IODINE AND FLUORINE ORGANIC BUDGETS

Species	Budgets			Percentage Source Contributions (%)	
	Northern Hemisphere	Southern Hemisphere	Global Average	Natural	Man-made
Cl	2.9 ppb	2.4 ppb	2.7 ppb	23	77
Br	10-30 ppt	--	--	50-90	50-10
I	<2 ppt	<2 ppt	<2 ppt	100	0
F	1.0 ppb	0.9 ppb	1.0 ppb	0	100

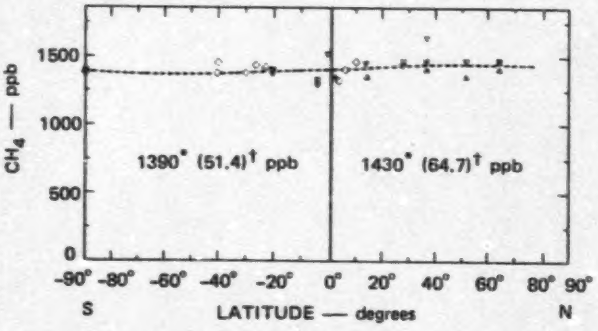
SECTION 15

ATMOSPHERIC HYDROCARBONS, CO, NO_x, PAN, AND O_3

A. Hydrocarbons

While these species were not of principal interest in this study, they were also measured at several urban and nonurban sites. The major reason for including hydrocarbons (HCs) was largely based on our finding of reduced HO levels in the troposphere. These low HO levels could allow some nonmethane hydrocarbons to enter the stratosphere. Since the Cl atom reaction with molecules such as C_2H_6 and C_2H_2 was 10^2 to 10^3 times faster than reaction with CH_4, we felt that nonmethane hydrocarbons could compete with CH_4 as a sink for Cl atoms.

Figure 29 shows the global distribution of CH_4 in the northern and southern hemispheres. The global distribution of CH_4 is essentially uniform with southern hemisphere levels, and about 3 percent lower than the northern hemisphere values. (Table 15 describes the polynomial used to fit the CH_4 global data.) The global average concentration of 1.41 ppm for CH_4 was also measured. Even though large man-made sources of CH_4 exist in the northern



*Average hemispheric concentration

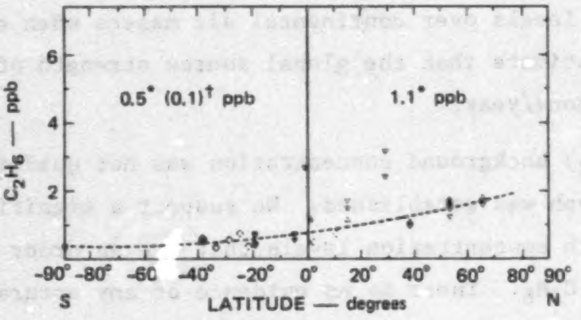
†Standard deviation

FIGURE 29 GLOBAL DISTRIBUTION OF METHANE

hemisphere, CH_4 is largely of natural origin with a high background and a long atmospheric lifetime. This long lifetime allows for a nearly uniform distribution of CH_4. While residence times of 2 to 20 years have been estimated for CH_4, our data are in good agreement with the highest values ($\tau_{CH_4} \approx 21$ years).

The next most ubiquitous hydrocarbon present in the global atmosphere was found to be C_2H_6. The global distribution of C_2H_6 was dissimilar to that of CH_4, probably because C_2H_6 has a much shorter tropospheric lifetime than CH_4 does. A third order polynomial is used to fit the C_2H_6 global distribution and is described in Table 15. Figure 30 shows the nonlinear C_2H_6 distribution in the northern hemisphere. At least in the southern hemisphere the concentration of C_2H_6 is relatively uniform, averaging about 0.5 ppb. In the northern hemisphere, however, the concentration approaches 2 ppb at mid-northern latitudes but drops off to nearly 1 ppb near the equator. The weighted average concentration of C_2H_6 that represents its burden in the northern hemisphere is calculated to be 1.1 ppb. Thus, a very large gradient of C_2H_6 between the northern hemisphere and southern hemisphere exists. The latitudinal profile of C_2H_6 suggests that there are significant sources in the northern hemisphere.

Figure 31 shows the diurnal variation of C_2H_6 at Point Arena (Site 11). The C_2H_6 background is 1.9 ppb and no diurnal variation is evident. The sources of C_2H_6 are complex but there is little doubt that both man-made and



*Average hemispheric concentration

†Standard deviation

FIGURE 30 GLOBAL DISTRIBUTION OF ETHANE

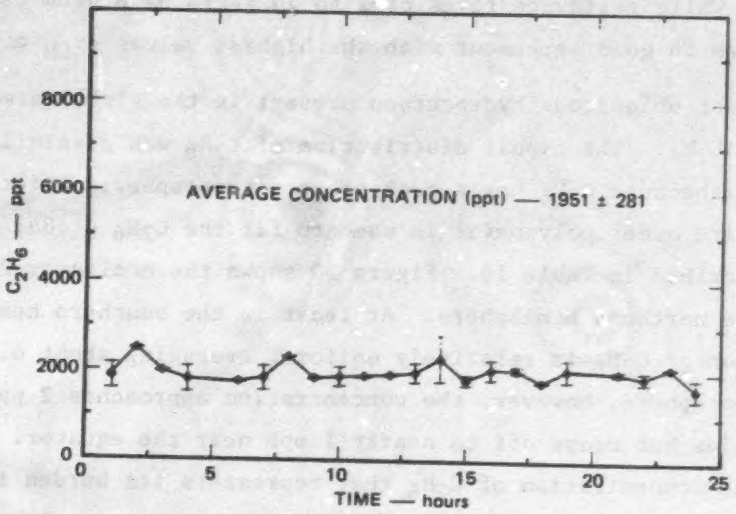


FIGURE 31 ETHANE DIURNAL VARIATIONS AT POINT ARENA (SITE 11)

natural sources exist. Figure 32 shows a much higher background of C_2H_6 at the Jetmore, Kansas site (Site 12). This region, while otherwise representative of background conditions, contains a large number of gas wells. We feel that C_2H_6 enhancement in this region is largely due to these sources. Measurements of C_2H_6 at other continental sites (Rasmussen et al., 1975) could suggest higher C_2H_6 levels over continental air masses when compared to marine environments. We estimate that the global source strength of C_2H_6 is approximately 10 million tons/year.

Acetylene (C_2H_2) background concentration was not quantified, but an upper limit of 0.2 ppb was established. We suspect a significant north-south gradient of C_2H_2 with concentration levels that are an order of magnitude lower than those of C_2H_6. There is no evidence of any natural sources of C_2H_2. Automobile exhaust is known to be a dominant source of C_2H_2.

We also attempted to measure global distribution of C_2H_4. These data have already been reported (Singh et al., 1978b) and were considered suspect because of possible contamination problems. The average northern hemisphere

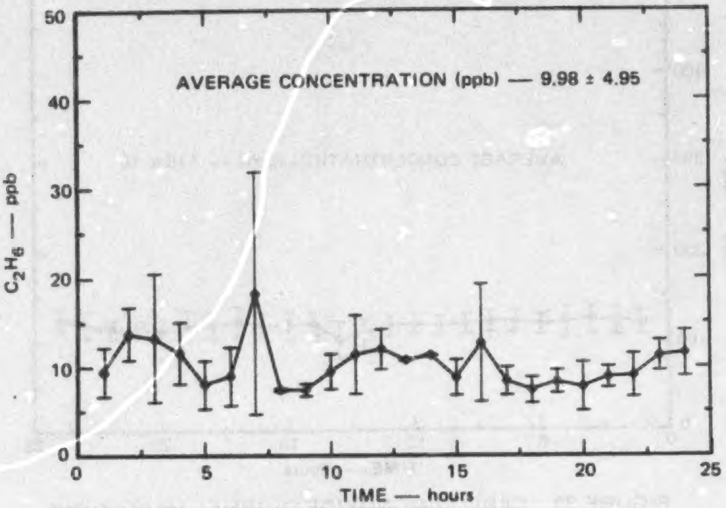


FIGURE 32 ETHANE DIURNAL VARIATIONS AT JETMORE (SITE 12)

and southern hemisphere concentrations of C_2H_4, for example, were measured to be 1.4 ± 1.1 ppb and 1.0 ± 0.6 ppb, respectively. In situ measurements at Sites 12 and 14 indicated average concentrations of only 0.3 ppb. We consider the latter to be more reliable. Additional in situ measurements must be conducted to determine if C_2H_4 is a ubiquitous component of the global atmosphere.

B. Carbon Monoxide

Carbon monoxide is a well-established component of the global atmosphere, and its global distribution and latitudinal gradients have been quite well characterized (Sieler, 1974). Our measurements point to additional features that may suggest a far more complex distribution of CO. Figures 33 and 34 show the diurnal variations of CO at two sites (Sites 11 and 12) that are located at roughly the same latitude but have different characteristics because of their marine (Site 11) and continental natures (Site 12). At Site 12 no diurnal variation of CO is observed and an average concentration of 175 ± 50 ppb was measured. Site 11, however, did show slightly lower values in the afternoon, but more importantly indicated CO levels of 118 ± 15 ppb.

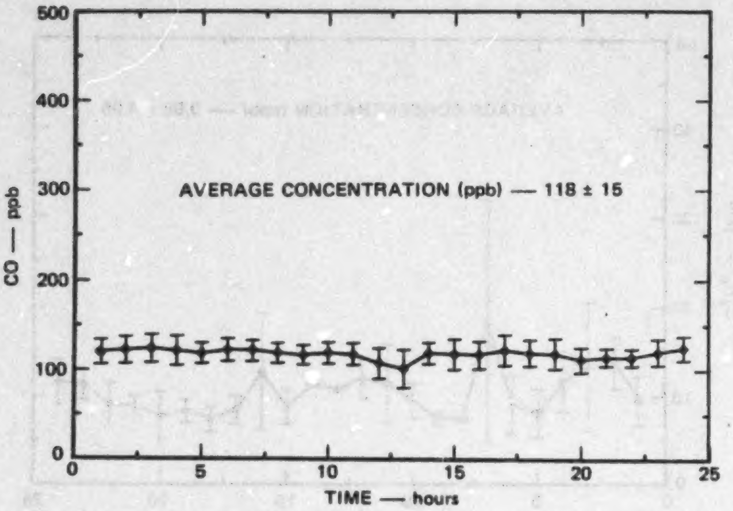


FIGURE 33 CARBON MONOXIDE DIURNAL VARIATIONS AT POINT ARENA (SITE 11)

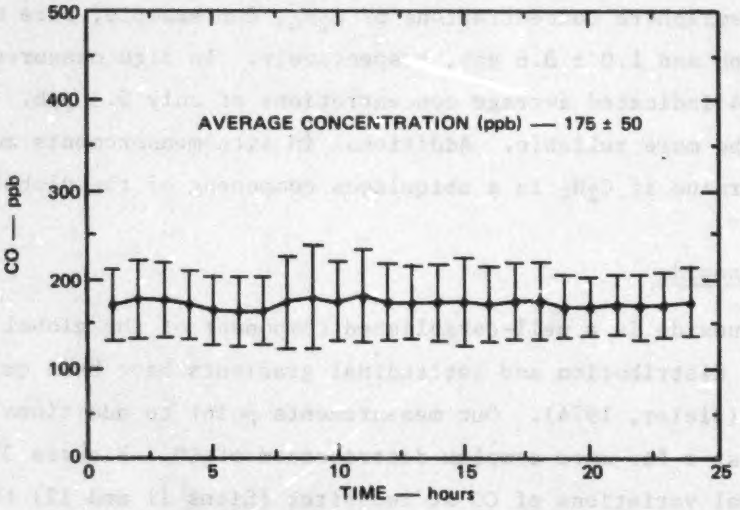


FIGURE 34 CARBON MONOXIDE DIURNAL VARIATIONS AT JETMORE (SITE 12)

A nearly 50 percent difference between Site 11 and Site 12 at roughly the same season (see Table 24) cannot be attributed to the slight difference in latitude. One could speculate that this gradient is because of a CO source on the North American continent. Similar differences between F-11 and F-12, which are indicators of authropogenic activity, were not observed. It is possible that continental land masses provide a large source of natural CO.

C. NO_x, PAN, and O_3

The NO and NO_2 levels we measured were typically less than 5 ppb each at clean sites (Table 24). While in principle the chemiluminescent instruments we used (see Table 9) had adequate sensitivity to measure 1 ppb of NO, we are unsure of the specificity of this detector. Since the current instrumentation cannot be considered very reliable at concentrations of less than 5 ppb, perhaps it would be more prudent to say that levels of NO and NO_2 in clean atmospheres were less than 5 ppb. Recent NO_x measurements of Noxon (1978) and McFarland (1979) suggest NO_x levels that are less than 0.1 ppb. NO levels of about 4 ppt have been measured by McFarland in the clean marine environment. The atmospheric abundance and the fate of NO_x in the free troposphere is poorly understood at present.

If McFarland's measurements are correct, it is possible that inorganic nitrogen is tied up and transported in an organic form. PAN is one such species. We have attempted to measure PAN at some of the clean remote sites. Figures 35 and 36 show the diurnal variations of PAN at Site 12 (clean continental) and Site 14 (clean marine). The higher levels of PAN (maximum of 0.5 ppb) at Site 12 were probably from the oxidation of alkanes. At Site 14 the levels were much lower. The data, however, were quite limited and general conclusions cannot be drawn. Meanwhile, if NO_x levels in the troposphere are indeed less than 20 ppt, as McFarland's data might suggest, organic nitrogen carriers such as PAN could play an important role in the nitrogen chemistry of the troposphere. From our data it would appear, however, that PAN levels in the troposphere are likely to be much less than 100 ppt (Table 24). Other organic nitrogen species (such as CH_3ONO_2) may also play a similar role.

Ozone was also measured at several sites at typical background concentrations of 30 to 60 ppb. The very short lifetime of O_3 does not allow any

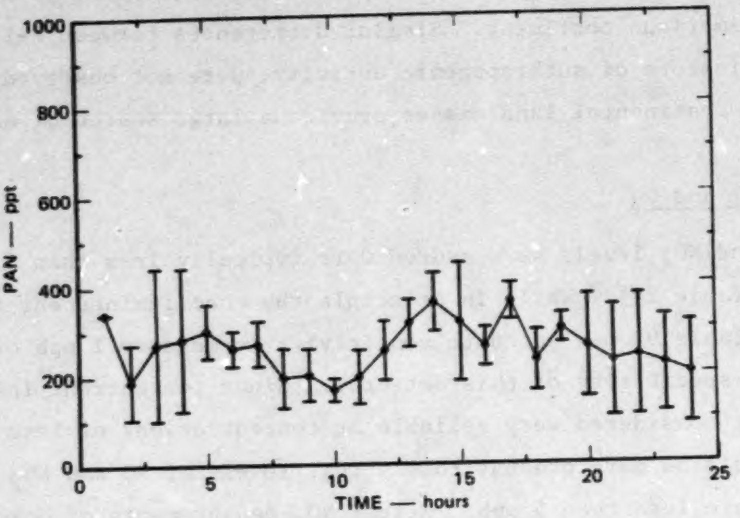


FIGURE 35 PAN DIURNAL VARIATIONS AT JETMORE (SITE 12)

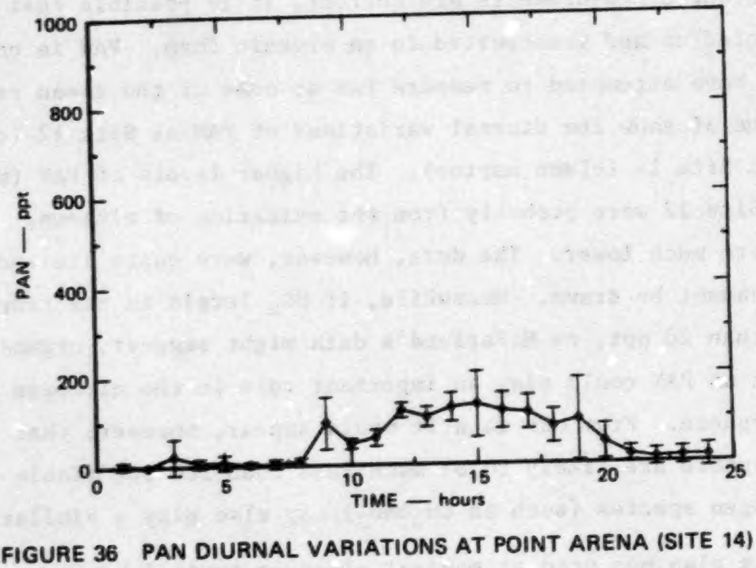


FIGURE 36 PAN DIURNAL VARIATIONS AT POINT ARENA (SITE 14)

general conclusions from our limited data. A much more extensive analysis of O_3 data from several remote sites in the northern hemisphere has already been presented by Singh et al. (1978c).

SECTION 16

BEST ESTIMATES OF THE MEAN RESIDENCE TIME OF SELECTED MOLECULES BASED ON THE PRESENT STUDY

The analysis of CH_3CCl_3 data supports an average tropospheric HO concentration of 3 to 4 × 10^5 molecules/cm^3. The role of HO as a primary removal mechanism for a number of atmospheric chemicals has already been discussed by a number of investigators (Singh, 1977a, 1977b; Weinstock et al., 1979). At this time a seasonally averaged HO abundance of 4 × 10^5 molecules/cm^3 in the troposphere is our best estimate and has been supported by other investigators (Crutzen and Fishman, 1977; Campbell et al., 1979). A weighted global average temperature of 265°K was used to estimate the average residence time of a large number of C_1 and C_2 molecules. The rate data for reaction with HO was taken from two sources (NASA, 1977; Hampson and Garvin, 1978). In some instances when no rate constants were available, it was possible to estimate these from theoretical considerations and from comparisons with similar molecules. Table 30 reports our best estimate of the mean tropospheric residence time of 20 selected molecules of atmospheric interest. It is worthwhile to add that, as a rule of thumb, the percentage of a given material released at ground level that will enter the stratosphere is roughly twice its residence time. As an example, 16.6 percent of CH_3CCl_3 released at ground level, according to Table 30, would enter the stratosphere, while only 1.2 percent of CH_2BrCH_2Br would. The residence times listed in Table 30 are optimized towards the tropospheric distribution of CH_3CCl_3. Residence times of species with significantly different global distributions could be subject to errors of ±50 percent because of the expected latitudinal gradients of HO in the troposphere.

Table 30

ESTIMATED TROPOSPHERIC RESIDENCE TIMES OF SELECTED MOLECULES

Molecule	HO Reaction Rate Constant at 265°K	Mean Residence Time[†] τ(years)
CH_3Cl	$2.96 \cdot 10^{-14}$	2.7
CH_2Cl_2	$8.38 \cdot 10^{-14}$	1.0
$CHCl_3$	$6.51 \cdot 10^{-14}$	1.2
$CHFCl_2$	$1.85 \cdot 10^{-14}$	4.3
CHF_2Cl	$2.28 \cdot 10^{-15}$	34.8
CH_2ClF	$2.42 \cdot 10^{-14}$	3.3
CH_3Br	$2.74 \cdot 10^{-14}$	2.9
CH_4	$3.70 \cdot 10^{-15}$	21.5
CO	$1.40 \cdot 10^{-13}$	0.6
CCl_2CCl_2	$1.02 \cdot 10^{-13}$	0.8
$CHClCCl_2$	$2.30 \cdot 10^{-12}$	0.04
CH_3CCl_3	$9.64 \cdot 10^{-15}$	8.3
CH_2ClCH_2Cl[*]	$1.41 \cdot 10^{-13}$	0.6
CH_3CHCl_2[*]	$1.71 \cdot 10^{-13}$	0.5
CH_3CH_2Cl	$2.57 \cdot 10^{-13}$	0.3
CH_3CF_2Cl	$1.57 \cdot 10^{-15}$	50.6
CH_2BrCH_2Br[*]	$1.41 \cdot 10^{-13}$	0.6
C_2H_6	$1.79 \cdot 10^{-13}$	0.5
COS	$5.60 \cdot 10^{-14}$[‡]	1.6
CS_2	$1.90 \cdot 10^{-13}$[‡]	0.4

[*] Rate constant with HO estimated from theoretical considerations.

[†] Based on an average HO abundance of 4 × 10^5 molecules/cm^3.

[‡] Calculated at 298°K.

SECTION 17

URBAN-NONURBAN RELATIONSHIPS OF MEASURED TRACE CONSTITUENTS

Because many of the trace constituents measured in this study are of man-made origin, a knowledge of their abundance in urban areas where the actual releases take place is a useful way to confirm the nature of the source. In addition, many of the trace constituents measured here are toxic and otherwise detrimental to human health. Since urban centers have high population densities, the need to characterize the urban atmospheres to establish the intake of a complex mixture of toxic chemicals clearly exists. Aware of the potential toxicity of several chemicals, we undertook a number of field studies in urban and suburban locations.

In Table 31 we have summarized data from all sites monitored during this study. As stated earlier, Site 6 was merged with Site 1 since only two pollutants were measured at Site 6 (CH_3Br and $COCl_2$) and were not measured at Site 1.

In Table 31 we present the maximum, minimum, and the average concentrations for each of the species. The quantity in parentheses is the standard deviation associated with the average concentration. The concentrations are based on hourly averages which were obtained from instantaneous measurements. In addition, we have presented an average daily outdoor dose for each of the species. The standard deviation associated with the daily dose is also reported based on the collected data. The daily outdoor dose is reported in μg/day and is calculated based on an air intake of 23 m^3/day at 25°C and 1 atm (NAS, 1978). Table 31 contains a great deal of information that is self-explanatory; therefore only salient observations will be made here. In the following sections we will discuss the urban-nonurban relationships of chemicals in three subgroups.

A. Chlorofluorocarbons and SF_6

None of the chlorofluorocarbons nor the SF_6 that we studied are known or suspected to be toxic at the concentrations that were measured. The following observations from Table 31 are pertinent:

- F-12 and F-11 maximum concentrations did not exceed 4.2 ppb. The highest average concentrations measured in urban environs were less than five times the background levels.
- F-113 and F-114 maximum concentrations did not exceed 1.2 and 0.2 ppb, respectively. The highest average concentrations were once again less than six times the background values.
- SF_6 maximum levels never exceeded 10 ppt.
- The combined concentration of all fluorocarbons, based on our data, should not exceed 10 ppb even in a highly polluted urban environment. The maximum dose of all fluorocarbons at typical urban-suburban sites should not exceed 250 μg/day. The typical daily doses for each fluorocarbon are listed in Table 31.

B. Halogenated (Nonfluorinated) Species

Unlike the chlorofluorocarbons, a number of the chlorinated hydrocarbons are suspected to be highly toxic. Once again we shall briefly discuss the levels of exposure to these chemicals.

- Typical CCl_4 average concentrations in urban areas were about 25 percent higher than background levels. This provides evidence for the existing urban sources of CCl_4 but also suggests that these sources are not very large. The maximum measured concentration of CCl_4 did not exceed 0.25 ppb. Because of the relatively uniform distribution of CCl_4, an average urban dose of 19 μg/day was calculated.
- Unlike CCl_4, wide fluctuations in the abundance of $CHCl_3$ were observed. The maximum concentration, however, never exceeded 0.8 ppb. Among all the sites monitored, the highest average dose of 13 μg/day was calculated for Site 8. Coastal water samples at Site 2 were found to contain very high levels of $CHCl_3$ (3 ppb of $CHCl_3$ in helium that was in equilibrium with water).
- Since both CCl_4 and $CHCl_3$ are suspected toxic chemicals, a combined 30 μg/day dose in urbanized areas is possible. This can be compared to a possible intake of 15 to 30 μg/day from drinking water (NAS, 1978). Thus, the intake of CCl_4 and $CHCl_3$ from the polluted atmosphere can approach or even exceed that from drinking water.
- The CH_2Cl_2 concentration did not exceed 2 ppb. The highest calculated average daily dose was 35 μg/day at Site 13, but typically it was much lower. The maximum average concentration at Site 13 was an order of magnitude larger than the background concentration of about 40 ppt.

- The maximum CH_3Cl concentration was less than 3 ppb. A typical daily dose was between 40 to 60 μg/day. As stated earlier, CH_3Cl is a constituent of the natural atmosphere but man-made sources do appear to be significant. In Lisbon, as in Los Angeles, the CH_3Cl concentrations were found to be almost 3 times the background levels.
- Methyl bromide levels in urban areas are definitely elevated, but natural sources may also exist. The highest CH_3Br concentration was less than 1 ppb (Site 3) although typical CH_3Br levels did not exceed 0.2 ppb. Among all the sites monitored, the highest dose was calculated for Los Angeles and was about 9 μg/day.
- The toxicity of CH_3CCl_3 is still in question (Farber, 1979). Concentrations as high as 8 ppb were measured. Among the various sites monitored, the highest average daily dose of 180 μg/day was measured at Los Angeles (Site 3).
- CH_2BrCH_2Br is a suspected carcinogen. Its levels, however, never exceeded 0.1 ppb. Since CH_2BrCH_2Br was only measured at a few sites, much higher urban concentrations can be expected.
- Maximum concentrations of CCl_2CCl_2 and $CHClCCl_2$ were 3.7 ppb and 3.1 ppb, respectively. Both of these species are suspected to be toxic and the latter has been identified as a potential carcinogen (Greenberg and Parker, 1979). The highest average daily dose for CCl_2CCl_2 and $CHClCCl_2$ was 170 μg/day (Site 8) and 45 μg/day (Site 13). respectively.
- $COCl_2$ was measured at several sites but the concentrations never exceeded 0.13 ppb. The average concentrations were considerably lower. Our data points to a dose that is always less than 5 μg/day. The distribution of $COCl_2$ is consistent with a photochemical secondary source. This source has been identified to be photooxidation of chloroethylenes, particularly CCl_2CCl_2 and $CHClCCl_2$ (Singh, 1976; Singh et al., 1977c).

C. N_2O, Hydrocarbons, CO, NO_x, and Ozone

The urban-nonurban relationships of these chemicals are self-evident from Table 31. The N_2O and the light hydrocarbons measured here are not suspected to be toxic. A great deal of literature on the distribution and effects of CO, NO_x, and O_3 is available in the literature (EPA, 1977).

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Table 31

URBAN-NONURBAN POLLUTANT RELATIONSHIPS: CONCENTRATIONS AND DAILY OUTDOOR DOSES OF CHE

Chemical Species	Site 1[*]		Site 2		Site 3		Site 4		Site 5		Site 7		Site 8		Site 9	
	Conc.[†]	Dose[‡]	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose
CCl_2F_2(ppt)	292(183) 750 162	38.6(19.2)	209(46) 578 163	23.7(2.4)	860(599) 2472 225	88.6(47.1)	633(606) 3382 209	71.3(27.1)	203(19) 262 162	23.4(0.8)	329(106) 673 214	38.6(7.4)	510(408) 2870 198	60.9(31.4)	269(83) 577 193	31.1(6.
CCl_3F(ppt)	129(62) 634 98	16.5(3.5)	119(34) 340 75	15.2(1.6)	622(534) 4207 115	74.7(29.3)	303(313) 1978 96	40.2(13.6)	116(5) 127 102	14.6(0.5)	187(32) 325 132	23.9(2.1)	500(504) 3300 122	59.1(31.9)	149(42) 338 80	17.8(3.
$CHClF_2$(ppt)	—	—	—	—	—	—	—	—	—	—	30 20	—	—	—	—	—
$CHCl_2F$(ppt)	—	—	—	—	61(75) 300 21	5.9(1.1)	26(5) 30 12	2.4(0.3)	14(5) 45 8	1.3(0)	—	—	—	—	—	—
CCl_2FCClF_2(ppt)	31(30) 137 8	6.4(4.3)	31(41) 450 12	5.6(1.8)	118(77) 315 29	19.5(9.0)	37(13) 105 21	6.4(0.8)	20(3) 31 11	3.4(0.5)	42(26) 181 17	7.2(3.0)	99(166) 1144 20	25.6(32.0)	27(26) 255 14	4.6(1.
$CClF_2CClF_2$(ppt)	—	—	—	—	46(37) 150 8	6.7(2.1)	32(30) 165 12	2.7(1.6)	—	—	13(4) 21 9	2.1(0)	53(56) 212 6	11.2(9.0)	9(4) 15 3	1.3(0.
SF_6(ppt)	2.7(2.4) 8.5 0.2	0.48(0.27)	0.2(0.0) 0.4 0.1	0.03(0)	1.0(0.9) 6.6 0.2	0.13(0.05)	0.6(0.3) 1.3 0.1	0.08(0.03)	0.2(0.03) 0.3 0.2	0.03(0)	0.4(0.02) 0.4 0.4	0.05(0)	0.9(1.4) 8.5 0.3	0.13(0.08)	0.4(0.3) 0.9 0.2	0.08(0.
CCl_4(ppt)	121(7) 156 105	17.3(0.3)	129(15) 184 91	18.6(1.3)	134(20) 204 106	18.9(1.6)	118(8) 144 106	17.3(1.3)	114(6) 133 98	16.5(0.5)	132(11) 186 102	18.9(0.8)	144(30) 199 99	20.7(0.3)	125(31) 226 87	17.3(2.
$CHCl_3$(ppt)	33(26) 217 12	3.7(0.8)	37(15) 114 15	4.3(0.8)	102(84) 724 23	10.6(4.3)	99(98) 616 23	11.4(4.0)	17(2) 24 12	1.9(0)	25(5) 36 4	2.9(0.3)	67(74) 310 24	12.5(12.8)	16(8) 38 2	1.9(0.
CH_2Cl_2(ppt)	—	—	—	—	—	—	—	—	—	—	55(14) 87 38	4.5(1.3)	111(94) 473 33	7.4(2.9)	44(25) 126 9	4.3(1.
CH_3Cl(ppt)	999(269) 1600 700	49.5(8.0)	1219(240) 1768 680	58.0(7.2)	834(80) 944 708	39.9(0)	1063(474) 2580 645	49.7(10.4)	713(51) 999 655	33.8(1.1)	728(192) 1320 392	35.6(5.3)	1490(728) 3811 566	69.2(21.3)	725(261) 1522 313	35.1(
CH_3I(ppt)	3(2) 11 1	0.5(0.3)	7(7) 44 1	1.1(0.5)	24(20) 120 5	2.9(1.1)	14(8) 49 3	1.9(0.5)	9(5) 33 3	1.3(0.5)	7(7) 23 0	1.1(0.5)	10(6) 26 1	1.3(0.5)	<1 <1 <1	—
CH_3Br(ppt)	16(2) 20 12	1.3(0.3)	71(37) 210 35	0.8(1.1)	108(138) 863 21	9.0(5.1)	24(11) 59 14	2.1(0.5)	5(3) 18 3	0.3(0.3)	25(6) 34 17	2.4(0.5)	45(40) 177 7	4.0(2.1)	8(6) 30 3	0.8(0.
CCl_3CCl_3(ppt)	—	—	—	—	—	—	—	—	—	—	6(1) 9 4	1.3(0)	20(9) 34 5	4.5(0)	6(3) 11 2	1.6(0.

[*] For a site description see Table 10.

[†] Concentration data expressed as average (standard deviation in parentheses), maximum, and minimum.

[‡] Daily outdoor dose expressed in μg/day and based on air intake of 23 m³/day at 25°C and 1 atmosphere pressure.

A

Table 31

TANT RELATIONSHIPS: CONCENTRATIONS AND DAILY OUTDOOR DOSES OF CHEMICAL SPECIES

	Site 7		Site 8		Site 9		Site 10		Site 11		Site 12		Site 13		Site 14	
se	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose
(0.8)	329(106) 673 214	38.6(7.4)	510(408) 2870 198	60.9(31.4)	269(83) 577 193	31.1(6.1)	240(31) 338 193	27.9(1.3)	220(20) 272 180	25.3(0.8)	254(18) 306 220	29.3(1.3)	974(417) 2059 304	12.5(26.9)	252(16) 297 222	28.7(0.8)
.5)	187(32) 325 132	23.9(2.1)	500(504) 3300 122	59.1(31.9)	149(42) 338 80	17.8(3.5)	145(19) 233 118	18.6(0.8)	126(13) 201 98	16.0(0.5)	138(6) 156 121	17.8(0.3)	541(307) 1794 151	71.0(25.)	152(19) 237 105	19.2(1.3)
—	30 20	—	—	—	—	—	—	—	—	—	27(13) 60 5	2.4(0.5)	148(197) 800 25	4.3(1.9)	—	4.3(1.9)
(0)	—	—	—	—	—	—	—	—	—	—	6(1) 8 4	0.8(0)	13(7) 35 5	1.3(0.3)	7(1) 9 3	0.8(0)
(0.5)	42(26) 181 17	7.2(3.0)	99(166) 1144 20	25.6(32.0)	27(26) 255 14	4.6(1.3)	19(6) 42 4	3.4(0.8)	23(6) 42 14	4.3(0.5)	23(5) 40 12	43.2(0.8)	76(68) 365 17	15.4(9.0)	22(2) 27 18	3.8(0.5)
—	13(4) 21 9	2.1(0)	53(56) 212 6	11.2(9.0)	9(4) 15 3	1.3(0.3)	9(4) 15 3	1.6(0.5)	12(5) 23 3	1.9(0.5)	12(3) 20 7	1.9(0.3)	26(32) 168 8	4.3(1.1)	13(3) 18 7	2.1(0.3)
(0)	0.4(0.02) 0.4 0.4	0.05(0)	0.9(1.4) 8.5 0.3	0.13(0.08)	0.4(0.3) 0.9 0.2	0.08(0.05)	0.3(0.1) 0.6 0.3	0.05(0)	0.3(0.04) 0.3 0.2	0.05(0)	0.4(0.1) 0.5 0.3	0.05(0)	4.0(2.0) 10.3 0.6	0.56(0.11)	0.3(0.1) 0.9 0.1	0.05(0.03)
(0.5)	132(11) 186 102	18.9(0.8)	144(30) 199 99	20.7(0.3)	125(31) 226 87	17.3(2.7)	127(18) 191 92	18.4(0.8)	123(8) 143 106	17.6(1.1)	128(12) 150 106	18.6(1.1)	133(17) 178 111	19.4(2.1)	125(8) 142 104	18.1(0.5)
(0)	25(5) 36 4	2.9(0.3)	67(74) 310 24	12.5(12.8)	16(8) 38 2	1.9(0.3)	13(4) 19 6	1.3(0.3)	20(5) 42 8	2.1(0.3)	16(5) 34 9	1.9(0.3)	—	—	18(6) 48 12	1.9(0.3)
—	55(14) 87 38	4.5(1.3)	111(94) 473 33	7.4(2.9)	44(25) 126 9	4.3(1.3)	52(22) 99 15	3.7(1.1)	45(22) 102 13	3.7(0.8)	54(15) 105 33	4.3(0.5)	401(352) 1920 60	33.3(12.8)	39(17) 80 16	3.2(0.5)
(1.1)	728(192) 1320 392	35.6(5.3)	1490(728) 3811 566	69.2(21.3)	725(261) 1522 313	35.1(10.4)	690(182) 1136 402	33.3(1.9)	730(134) 1213 498	35.9(4.3)	586(64) 760 503	27.9(0.8)	897(456) 2444 326	43.6(8.0)	629(50) 847 534	30.1(1.3)
(0.5)	7(7) 23 0	1.1(0.5)	10(6) 26 1	1.3(0.5)	<1 <1 <1	—	<1 <1 <1	—	5(3) 16 2	0.8(0.3)	2(1) 5 1	0.3(0.3)	3(2) 8 1	0.5(0.3)	3(2) 10 1	0.5(0.3)
(0.3)	25(6) 34 17	2.4(0.5)	45(40) 177 7	4.0(2.1)	8(6) 30 3	0.8(0.3)	5(2) 10 2	0.5(0)	20(6) 32 11	1.9(0.3)	5(1) 9 4	0.5(0)	31(31) 160 4	2.9(0.8)	13(5) 36 7	1.1(0.3)
—	6(1) 9 4	1.3(0)	20(9) 34 5	4.5(0)	6(3) 11 2	1.6(0.8)	5(1) 8 4	1.3(0.3)	7(1) 8 3	1.6(0.3)	6(2) 10 2	1.1(0.3)	—	1.1(0.3)	—	1.1(0)

B

Table 31 (Continued)

Chemical Species	Site 1*		Site 2		Site 3		Site 4		Site 5		Site 7		Site 8		Site 9
	Conc.†	Dose‡	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.
CH_3CCl_3(ppt)	141(117) 563 70	18.6(10.9)	111(27) 212 61	13.8(2.1)	1545(1538) 7663 100	177.4(109.6)	159(75) 454 75	19.7(4.0)	104(9) 126 73	12.8(0.5)	313(130) 895 107	39.9(10.4)	834(560) 3012 282	98.4(35.4)	231(56) 342 130
CH_2BrCH_2Br(ppt)	—	—	—	—	—	—	—	—	—	—	10(5) 23 5	0.5(0.2) 1.3(0.5)	23(19) 92 4	2.8(0.2) 7.4(0.5)	<4 <4 <4
CCl_2CCl_2(ppt)	194(388) 2490 16	37.2(43.1)	214(425) 3702 17	31.4(20.7)	722(527) 2267 71	130.1(58.8)	279(231) 1153 18	45.5(14.6)	31(10) 77 15	4.0(0.5)	65(49) 290 20	10.4(4.8)	983(454) 2325 96	168.6(42.8)	29(5) 39 22
$CHClCCl_2$(ppt)	93(323) 3097 6	13.8(12.8)	24(14) 64 0	1.6(1.1)	315(310) 1772 26	34.6(22.6)	35(50) 444 6	3.7(2.4)	15(3) 22 8	0.5(0.3)	26(19) 90 9	2.9(1.3)	266(94) 476 57	34.6(4.3)	13(1) 16 10
$COCl_2$(ppt)	30(3) 39 28	2.9(0.3)	—	—	31(7) 55 22	2.9(0.5)	29(6) 44 17	2.9(0.3)	22(5) 29 13	1.9(0.3)	18(8) 36 6	1.6(6.5)	45(20) 121 17	4.0(0.5)	13(4) 18 8
N_2O(ppb)	299(11) 320 279	12768(383)	310(14) 383 256	13151(360)	313(17) 349 272	13406(511)	310(13) 342 275	13236(255)	312(18) 352 283	13279(638)	310(15) 356 276	13194(298)	538(266) 1558 290	25408(10257)	323(46) 487 286
NO(ppb)	9(13) 91 1	226(112)	—	—	47(46) 226 6	1381(875)	17(6) 36 2	479(112)	1(1) 5 0	56(29)	9(5) 23 0	253(112)	13(12) 87 4	338(141)	1(1) 3 0
NO_2(ppb)	19(13) 83 5	819(473)	5(2) 13 2	215(43)	57(35) 218 11	2413(862)	17(11) 53 1	732(173)	1(1) 7 0	43(43)	4(5) 41 0	130(85)	27(15) 61 4	1162(431)	—
PAN(ppt)	—	—	—	—	—	—	—	—	—	—	299(192) 826 91	29.4(9.8)	1610(1452) 5656 255	233(146.2)	127(61) 224 48
PPN(ppt)	—	—	—	—	—	—	—	—	—	—	43(24) 105 14	5.0(1.5)	337(385) 1820 70	51.4(33.3)	54(22) 91 25
O_3(ppb)	29(8) 44 12	1349(226)	29(8) 51 11	1349(181)	38(53) 213 0	1484(809)	49(24) 104 1	2202(181)	53(12) 78 28	2383(314)	38(6) 55 23	1708(181)	37(31) 124 0	1708(540)	46(3) 54 37
CO(ppb)	204(388) 2443 60	4700(1891)	132(191) 1720 60	3236(1314)	1531(1288) 5740 85	40362(26805)	359(262) 1520 85	9084(3203)	—	—	204(113) 1245 103	5224(1234)	766(425) 2597 143	19506(7246)	—
CH_4(ppb)	1353(105) 2131 1287	20253(369)	1417(53) 1623 1090	21229(450)	2302(832) 5202 1402	32795(7892)	1858(312) 3043 1276	28039(2820)	1414(38) 1637 1342	21288(359)	1459(43) 1760 1300	21857(359)	1648(150) 2033 1073	24573(1306)	—

*For a site description see Table 10.

†Concentration data expressed as average (standard deviation in parentheses), maximum, and minimum.

‡Daily outdoor dose expressed in ug/day and based on an air intake of 23 m^3/day at 25°C and 1 atmosphere pressure.

A

Table 31 (Continued)

	Site 7		Site 8		Site 9		Site 10		Site 11		Site 12		Site 13		Site 14	
ose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose
(0.5)	313(130) 895 107	39.9(10.4)	834(560) 3012 282	98.4(35.4)	231(56) 342 130	28.7(5.3)	143(22) 178 84	18.1(1.3)	111(18) 150 83	13.8(1.1)	130(16) 159 106	16.2(0.8)	789(649) 2931 150	102.7(42.3)	132(11) 158 115	16.5(0.8)
	10(5) 23 5	0.5(0.2) 1.3(0.5)	23(19) 92 4	2.8(0.2) 7.4(0.5)	<4 <4 <4	—	<4 <4 <4	—	5(1) 7 4	0.3(0) 0.8(0)	—	—	—	—	—	—
(0.5)	65(49) 290 20	10.4(4.8)	983(454) 2325 96	168.6(42.8)	29(5) 39 22	4.5(0.5)	32(3) 39 22	5.1(0)	34(5) 48 20	5.6(0.5)	41(10) 72 24	6.4(1.1)	1139(415) 1610 450	178.3(0)	34(11) 85 15	5.1(1.1)
(0.3)	26(19) 90 9	2.9(1.3)	266(94) 476 57	34.6(4.3)	13(1) 16 10	1.6(0)	12(2) 16 6	1.6(0)	11(1) 12 10	1.6(0)	13(4) 21 7	1.6(0)	417(425) 2192 48	44.2(21.5)	17(7) 34 8	1.9(0.5)
(0.3)	18(8) 36 6	1.6(6.5)	45(20) 121 17	4.0(0.5)	13(4) 18 8	1.3(0)	15(7) 28 2	1.1(0.5)	15(4) 21 9	1.3(0.3)	—	—	—	0.5(0.1)	15(5) 25 10	1.3(0.3)
(638)	310(15) 356 276	13194(298)	538(266) 1558 290	25408(10257)	323(46) 487 286	13364(724)	305(19) 335 269	13066(340)	313(8) 331 299	13236(213)	311(5) 321 296	3236(43)	313(8) 334 293	13364(85)	312(6) 327 299	13279(43)
(29)	9(5) 23 0	253(112)	13(12) 87 4	338(141)	1(1) 3 0	8(11)	3(1) 8 0	85(29)	2(2) 6 0	19(19)	1(2) 11 0	29(29)	—	—	3(3) 22 0	85(29)
(43)	4(5) 41 0	130(85)	27(15) 61 4	1162(431)	—	—	1(0) 1 0	16(0)	4(6) 64 2	215(85)	3(2) 15 0	130(43)	—	—	8(5) 31 0	346(173)
	299(192) 826 91	29.4(9.8)	1610(1452) 5656 255	233(146.2)	127(61) 224 48	13.1(7.1)	111(51) 261 35	12.5(1.9)	—	—	253(103) 520 100	28.4(5.8)	918(255) 1300 650	10.5(0)	80(57) 281 1	6.1(2.3)
	43(24) 105 14	5.0(1.5)	337(385) 1820 70	51.4(33.3)	54(22) 91 25	6.2(2.8)	40(16) 88 21	5.0(0.4)	—	—	—	—	76(38) 126 35	9.6(0)	—	—
(314)	38(6) 55 23	1708(181)	37(31) 124 0	1708(540)	46(3) 54 37	2067(90)	39(10) 56 10	1798(269)	35(6) 45 0	575(136)	31(11) 53 0	349(359)	—	—	—	—
	204(113) 1245 103	5224(1234)	766(425) 2597 143	19506(7246)	—	—	148(27) 328 108	3913(210)	118(15) 144 65	3149(314)	—	—	—	—	—	—
(359)	1459(43) 1760 1300	21857(359)	1648(150) 2033 1073	24573(1306)	—	—	1649(134) 2020 1447	24738(1830)	1479(19) 1513 1440	22203(240)	1600(80) 2700 1300	24004(1200)	—	—	1563(284) 3800 1467	27784(9648)

B

Table 31 (Concluded)

Chemical Species	Site 1[a]		Site 2		Site 3		Site 4		Site 5		Site 7		Site 8		Site 9		
	Conc.[†]	Dose[‡]	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.
C_2H_2(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	4512(2467) 9063 673	92.3(45.2)	331(179) 900 <200	9.8(3.5)	—
C_2H_4(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
C_2H_6(ppt)	—	—	—	—	—	—	—	—	—	—	2049(525) 3225 1598	59.9(0.5)	8393(3574) 15903 3067	199.2(80.6)	3102(1171) 7581 1952	87.0(13.6)	2239(4 3320 1009
C_3H_8(ppt)	—	—	—	—	—	—	—	—	—	—	<250 <250 <250	—	5902(1733) 10108 3173	233.3(61.4)	427(703) 3587 <250	16.2(8.8)	300(1 1140 <250
C_3H_6(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
nC_4H_{10}(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
iC_4H_{10}(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
nC_5H_{12}(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
iC_5H_{12}(ppt)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[a] For a site description see Table 10.

[†] Concentration data expressed as average (standard deviation in parentheses), maximum, and minimum.

[‡] Daily outdoor dose expressed in μg/day and based on an air intake of 23 m^3/day at 25°C and 1 atmosphere pressure.

A

Table 31 (Concluded)

7	Site 8		Site 9		Site 10		Site 11		Site 12		Site 13		Site 14	
Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose	Conc.	Dose
--	4512(2467) 9063 673	92.3(45.2)	331(179) 900 <200	9.8(3.5)	--	--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--	383(302) 2756 <200	11.7(2.9)	6796(7665) 47775 525	193.1(87.8)	--	--
.9(0.5)	8393(3574) 15903 3067	199.2(80.6)	3102(1171) 7581 1952	87.0(13.6)	2239(458) 3320 1009	66.0(5.3)	1951(281) 3007 1391	56.9(3.7)	9980(4950) 41300 5175	298.5(61.4)	14207(9068) 52050 3262	415.5(64.4)	1595(986) 8400 770	46.8(11.7)
--	5902(1733) 10108 3173	233.3(61.4)	427(703) 3587 <250	16.2(8.8)	300(188) 1140 <250	12.0(3.7)	450(165) 714 <250	19.4(5.1)	5485(7623) 71442 1755	217.1(119.2)	4323(4577) 19440 216	178.8(59.6)	510(376) 1966 <200	17.0(8.5)
--	--	--	--	--	--	--	--	--	115(89) 535 <200	4.0(4.0)	2449(2123) 14280 297	95.8(23.9)	--	--
--	--	--	--	--	--	--	--	--	3386(4306) 40687 875	178.8(95.0)	8156(6143) 26250 1563	452.5(111.7)	573(258) 1312 219	11.2(5.6)
--	--	--	--	--	--	--	--	--	1199(1381) 12763 234	61.4(27.9)	3236(3580) 25058 421	184.3(50.3)	--	--
--	--	--	--	--	--	--	--	--	775(775) 7158 151	48.4(20.7)	4265(5419) 35299 758	290.5(110.7)	--	--
--	--	--	--	--	--	--	--	--	731(873) 8127 129	48.4(20.7)	6641(6410) 47343 645	449.5(145.2)	--	--

B

SECTION 18

RECOMMENDATIONS FOR FUTURE RESEARCH

While a great deal about the budgets and fates of chlorinated species has been learned over the past three years, the data base has been less than sufficient to quantify the biospheric sources and sinks of several species. Spot measurements have not been adequate to determine if seasonal variations of species even exist. Considerable disagreement over the global distribution of both reactive and unreactive species exists. The past research can adequately be characterized as work of an exploratory nature.

The best method for understanding and controlling global pollution would require long-term measurements of chemical species in the free troposphere in both hemispheres. Continuous measurements at fixed stations can provide the high precision that is essential to quantifying tropospheric perturbations of man-made as well as natural species. A minimum set would require two stations in the northern hemisphere and another two in the southern hemisphere. The scope of measurements at these stations could be expanded as needs arose. The characterization of global pollution from a single site, while qualitatively useful, does not allow for quantitative analysis of sources and sinks.

Interhemispheric profiles of important trace constituents (such as CH_3CCl_3 and CH_2Cl_2) need to be better characterized to ascertain seasonal variations in the global distribution of these species. Such latitudinal profiles can be used to confirm possible asymmetries in the hemispheric HO distribution and the reasons for such asymmetries. These also provide an essential means for validating global 2-dimensional models that are currently in a state of active development. The possibility exists that species such as CH_2Cl_2 could be used to understand seasonal variations of HO in the natural atmosphere.

The ocean appears to be a major source of methyl halides and N_2O. Very little oceanic data on methyl halides is available. It is still unknown whether ocean fluxes of methyl halides and N_2O have any seasonal fluctuations. The role of oceans as sources or sinks of N_2O remains unresolved for lack of an extensive data base. The bromine and iodine atmospheric distributions and budgets are at best poorly understood. A number of trace constituents measured in the clean atmosphere are also toxic. The urban abundances of these and other toxic chemicals need to be characterized to determine population exposure.

SECTION 19

GENERAL OBSERVATIONS

We concluded that the atmosphere is contaminated by a large number of man-made chemicals that have never existed in nature. These man-made chemicals interfere with the chemistry and radiation balance of the atmosphere with potentially deleterious consequences. Fully three-quarters of the chlorine in the atmosphere is attributable to man-made activities. In many cases, nature appears to have no means to cleanse itself of pollutants in a harmless fashion.

It appears that fluorocarbons are increasing rapidly in the global atmosphere. The only removal mechanism appears to be photolytic destruction in the stratosphere. Unfortunately, the products of these fluorocarbons (chlorine atoms) can catalytically destroy stratospheric ozone. This could cause an increase in the rate of skin cancer as well as other unknown climatic effects.

Halocarbons do, however, serve a beneficial purpose. We have used them to study the dynamics of the atmosphere as well as the fundamental removal processes that are operative. We found that removal mechanisms in the gas phase are almost an order of magnitude slower than previously believed. The chances that man's activities are further reducing the scavenging ability of the natural atmosphere are evident.

Nitrous oxide, unlike halocarbons, is found to have major sources in ocean waters and does not appear to be changing. Nitrous oxide, as well as most halocarbons, absorbs infrared radiation. These chemicals have the potential to exacerbate the warming that may be caused by excessive CO_2.

Because of significant man-made sources of halocarbons, levels in urban areas are one to two orders of magnitude higher than in clean environments. It is further becoming apparent that many of these chemicals are toxic and carcinogenic, thus compounding their potential harmful effects.

LIST OF PUBLICATIONS

The following reports and articles have been published to date from the results of this study.

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16. ABSTRACT

Global distributions of a large number of halocarbons, hydrocarbons, SF_6 and N_2O are presented. These data are complemented with measurements in the polluted environments to establish urban-nonurban relationships and daily doses of these species. Measurements conducted over a 3-year period show that the atmospheric burdens of CCl_2F_2, CCl_3F, and CH_3CCl_3 are increasing rapidly. The growth of CCl_4 is small and that of N_2O is essentially undetectable. Long residence times of CCl_2F_2 and CCl_3F rule out the existence of any major removal processes in the troposphere. The global distribution of CCl_2F_2 and CCl_3F is used to calculate a fast interhemispheric exchange rate of 1.2 years. CCl_4 was shown to have an important oceanic sink, while both CH_3Cl and N_2O have a major source in the ocean. CH_3CCl_3 atmospheric data was used to demonstrate that its long residence time makes it a potential depletor of stratospheric ozone. The hydroxyl radical concentration in the troposphere was shown to be significantly lower ($\approx 4 \times 10^5$ molec./cm^3) than previously believed and probably asymmetric in the two hemispheres. Measurements show that the troposphere contains slightly under 3 ppb of organic Cl and about 77 percent of this is of man-made origin. The organic Br and I abundances are much lower and much less certain. The troposphere contains about 1 ppb of organic F and all of it appears to be man-made.

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